

BIOLOGICAL OXIDATION AND REDUCTION OF INORGANIC COMPOUNDS OF SULFUR

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The biological processes involved in the oxidation and reduction of inorganic compounds of sulfur are generally represented by the idealized "biological sulfur cycle" shown in Figure 1 (18). Sulfate and sulfide are pivotal compounds in the scheme as they represent both the most common forms of inorganic sulfur found in nature and are the most common forms of sulfur incorporated into biological materials. At the top of the scheme, the biosynthetic reactions involving the incorporation of sulfate as ester linkages into carbohydrates, lipids, phenol, steroids, etc. (14) are indicated as sulfation reactions. Sulfation reactions are extensively involved in the biosynthesis of structural components in plants and animals but sulfate esters have only rarely been reported to occur in bacteria. All three groups of organisms do have sulfatases which specifically hydrolyze the various esters. On the right hand portion of the scheme, the eight electron reduction of SO_4^{2-} to S^{-2} is represented and, at the bottom of the scheme, the biosynthesis of amino acids and cofactors (or vitamins) from S^{-2} is shown. On the left hand portion of the scheme, the oxidation of reduced sulfur compounds is indicated (shown here as sulfide but other common substrates include $\text{S}_2\text{O}_3^{2-}$ and elemental sulfur). The biological aspects of inorganic sulfur metabolism thus provide the essential transformations for the incorporation of sulfur into biological materials and a link between the appropriate geological and biological phenomena.

The oxidative and reductive process have been further classified depending on the organisms and the physiological significance of the process in their metabolism. Two physiological types of sulfate reduction are recognized (21). The first is assimilatory or biosynthetic sulfate reduction in which organisms reduce only enough sulfate to meet their nutritional requirements for sulfur. This pathway is considered to be in the pathway for the biosynthesis of cysteine and is usually under both coarse and fine metabolic regulation (29). Animals do not classically reduce sulfate and must depend upon plants and bacteria for their metabolites containing reduced sulfur. This pathway occurs in most plants and bacteria, including aerobes and anaerobes, and, because of its wide occurrence, is probably the largest biological process for the reduction of sulfate; however, only indirectly during the digestion and hydrolysis of biological materials does this pathway produce sulfide in nature. The second sequence involved in the reduction of sulfate is the dissimilatory or respiratory pathway of sulfate reduction in which sulfate in the absence of oxygen serves as a terminal electron acceptor for anaerobic respiration (13). This pathway of sulfate reduction occurs only in the sulfate-reducing bacteria, species of Desulfovibrio (25) and Desulfotomaculum (4), and results in the formation of very large amounts of S^{-2} . Respiratory sulfate reduction is the process responsible for the formation and accumulation of most S^{-2} in nature and is believed to be involved in many geochemical phenomena. The enzymes of the respiratory pathway are constitutive, i.e. not effected by growth conditions, and the intermediates and enzymes responsible for respiratory sulfate reduction are quite different from those involved in biosynthetic sulfate reduction. Members of the genus, Desulfovibrio are the most extensively studied of the sulfate-reducing bacteria. These bacteria have only a limited capability for oxidizing substrates (H_2 , formate, pyruvate, lactate, ethanol, fumarate) and are the first non-photosynthetic anaerobes in which c-type cytochrome were discovered (24). They also produce many low molecular weight electron carriers (13) and oxidative phosphorylation has been demonstrated to be coupled to electron transfer (19).

Most plants, bacteria and animals are capable of oxidizing reduced inorganic and organic compounds of sulfur to sulfate. Thus, a specific requirement of sulfate for growth has never been reported although it is extensively involved in essential biosynthetic reactions in plants and animals. Reduced sulfur compounds can also be utilized by microorganisms as electron donors for both aerobic and anaerobic growth, as well as photosynthetic growth with the formation of sulfate. Members of the genus, *Thiobacillus*, oxidize S^{-2} , $S_2O_3^{2-}$ and S^0 to SO_4^{2-} in the presence of oxygen and gain energy for growth in the form of adenosine triphosphate (ATP) by means of oxidative phosphorylation (32). One species, *T. denitrificans* can utilize either oxygen or nitrate with the formation of N_2 as terminal electron acceptor. Photosynthetic bacteria, members of the *Chromatiaceae* (purple sulfur bacteria) and *Chlorobiaceae* (green sulfur bacteria) can use reduced sulfur compounds as electron donors for photosynthetic growth first with the formation of S^0 and subsequently SO_4^{2-} . Although the biological sulfur cycle generally involves a large number of diverse organisms, it is possible to construct a simple, light-driven sulfur cycle by means of a sulfate-reducing bacterium and a photosynthetic bacterium. This is not a primary producing system, as water can not serve as a source of electrons, but it provides a model system for the study of the interactions required for the biological sulfur cycle. In addition, this simple form of the cycle may represent a primitive system for the conversion of solar energy into biologically useable energy.

In most soils and natural environments, there is a continuous flux of sulfur through the biological sulfur cycle without the accumulation of intermediates or significant changes in the concentrations of sulfate and sulfide. This situation can then be regarded as an uninterrupted or continuous sulfur cycle. Under certain conditions, one or more steps in this sulfur cycle can become inhibited with the result that the concentrations of sulfate and sulfide are drastically altered, often with dramatic effects on a specific environment. This can be considered to be an interrupted or discontinuous sulfur cycle and its consequences will be briefly considered. Under anaerobic conditions, the oxidation of reduced sulfur compounds is inhibited (except in the presence of NO_3^{-1}) and, with SO_4^{2-} , organic electron donors or H_2 and an environmental pH above 4.5, copious amounts of S^{-2} can be produced by the sulfate reducing bacteria. The consequences of this microbial reduction of sulfate to an environment are complex but can be largely analyzed in terms of the chemical properties of H_2S . Sulfide is an inhibitor of cytochrome oxidase which is essential for aerobic respiration, reacts with molecular oxygen and generates a reducing environment because of its low E_u value of about -300 mV. Thus, its formation in any environment can result in the formation of anaerobic conditions and the inhibition of aerobic flora. Sulfide also combines with heavy metals present in an environment to form insoluble sulfides and there is some evidence to indicate that most pyrite ores are formed from biologically produced sulfide. The black color of anaerobic environments is due to this reaction and the Black Sea is claimed to derive its name from the fact that in areas it appears to be black due to the abundance of FeS . As indicated previously, sulfide and elemental sulfur can serve as substrates for the growth of many microorganisms and on the periphery of an environment in which there is extensive sulfate reduction (termed a "sulfuretum") one can often find high concentrations of *Thiobacilli* and/or photosynthetic bacteria. For example, in very shallow marine environments, it is common to observe red and green photosynthetic bacteria growing on the surface of sediments that are producing S^{-2} . This phenomenon is made possible in part because at physiological pH values, H_2S is volatile and a sulfuretum can usually be detected by our olfactory senses. The volatility of H_2S formed by sulfate reduction can also result in an environment becoming extremely alkaline and it has been postulated to be the cause of the formation of certain deposits of Na_2CO_3 by the absorption of CO_2 from the atmosphere. The concentration of sulfate can be decreased in natural waters to the point that respiratory sulfate reduction ceases and interactions with methanogenic bacteria become important as will be discussed later. The sulfate-reducing bacteria have high levels of the enzyme hydrogenase concentrated around the periphery of their cells (18) and the enzyme

appears to be important both in the production and utilization of molecular hydrogen which is commonly found in anaerobic environments. The ability to utilize extremely low concentrations of H_2 has been postulated to be the role of the organisms in the rapid anaerobic corrosion of iron (9). The various environmental aspects of respiratory sulfate reduction are summarized in Table 1 and most of these environmental

TABLE 1: Environmental Effects of Respiratory Sulfate Reduction

1. Formation of Sulfide
2. Change of pH
3. Removal of Heavy Metals
4. Removal of Hydrogen
5. Removal of Sulfate
6. Changes in Microflora
7. Fractionation of Sulfur Isotopes

effects of respiratory sulfate reduction can be interpreted in terms of the chemical, biological and physical properties of H_2S . Postgate (23) has presented a more detailed and extensive discussion of these environmental effects of sulfate reduction. A related aspect of these bacteria is the fractionation of sulfur isotopes occurring during the reduction of sulfate which allows determination as to whether a given deposit of reduced sulfur was formed by geological phenomena or biological agents (34).

Under aerobic conditions, the absence of organic electron donors and/or acidic pH values (below 4.5) respiratory sulfate reduction is inhibited and a second type of imbalance in the biological sulfur cycle created which leads to the formation of very acidic environments (to pH 1.0). For this situation to occur, the presence of reduced sulfur compounds, such as H_2S , S^0 or $S_2O_3^{2-}$, which can be oxidized by the Thiobacilli to sulfate as H_2SO_4 , is required. In contrast to the sulfate-reducing bacteria which require fixed carbon, these organisms can utilize CO_2 as their sole source of carbon (35). This acidic environment occurs particularly where there is poor drainage and its formation can inhibit the growth of a wide variety of soil bacteria. From an economic point of view, these microorganisms can be important agents in the erosion of various types of stone and this aspect is emphasized by one isolate of these bacteria being named T. concretivorus (17). In general, the various physiological types of microorganisms responsible for the oxidation and reduction of inorganic sulfur compounds have been isolated in pure culture and their physiology studied sufficiently to predict and control the accumulation of sulfide and sulfate in a given environmental situation.

The biochemistry of the reactions of inorganic sulfur compounds has been only sporadically studied but although not all of the enzyme and reactions have been completely characterized, the reactions involved can at least be reasonably well outlined. Sulfate is first transported across the membrane of the cell by means of an active process involving sulfate-binding proteins (16) and once inside the cell universally reacts with ATP to form adenylyl sulfate (APS) and inorganic pyrophosphate (PP_i) as shown in Table 2, reaction 1. The equilibrium of the reaction lies in the direction of ATP and SO_4^{2-} and, for significant formation of APS, the reaction must be coupled to either or both pyrophosphate hydrolysis, Table 2, reaction 2, or phosphorylation in the 3'-position to form 3'-phosphoadenylyl sulfate (PAPS), Table 2, reaction 3. PAPS serves as the substrate for all sulfation reactions, Table 2, reaction 4, and forms a sulfate ester and 3',5'diphosphoadenosine (PAP), but specific enzymes, termed sulfotransferases, are required for the various acceptors such as alcohols, phenols, steroids, etc. PAPS is also believed to be the form in which SO_4^{2-} is reduced to SO_3^{2-} by the reduced triphosphopyridine nucleotide (TPNH₂) specific PAPS reductase Table 2, reaction 5; but, the role of this enzyme and that of the TPNH₂: sulfite reductase, Table 2, reaction 6, which catalyzes the 6 electron of SO_3^{2-} to S^{2-} in the biosynthetic pathway has recently been questioned (30). However,

it remains clear that the biosynthetic pathway is biochemically distinct from the respiratory pathway.

TABLE 2: The Enzymes of Biosynthetic Sulfate Reduction

1. ATP:sulfurylase

$$\text{ATP} + \text{SO}_4^{2-} \xrightarrow{\text{Mg}^{+2}} \text{APS} + \text{PP}_i \quad (28)$$
2. Inorganic pyrophosphatase

$$\text{PP}_i + \text{H}_2\text{O} \xrightarrow{\text{Mg}^{+2}} 2\text{P}_i \quad (28)$$
3. APS:kinase

$$\text{ATP} + \text{APS} \xrightarrow{\text{Mg}^{+2}} \text{PAPS} + \text{ADP} \quad (27)$$
4. Sulfotransferase

$$\text{ROH} + \text{PAPS} \rightarrow \text{ROSO}_3^{-1} + \text{PAP} \quad (14)$$
5. PAPS reductase

$$\text{PAPS} + \text{TPNH}_2 \rightarrow \text{SO}_3^{2-} + \text{PAP} + \text{TPN} \quad (37)$$
6. Sulfite reductase

$$\text{SO}_3^{2-} + 3\text{TPNH}_2 + \text{S}^{-2} + 3\text{TPN} + 3\text{H}_2\text{O} \quad (31)$$

The initial step in the respiratory pathway of sulfate reduction is the same as that in the biosynthetic pathway, that is, the formation of APS from ATP and SO_4^{2-} by ATP sulfurylase and its formation is coupled only to the hydrolysis of inorganic pyrophosphate, Table 2 and 3, reactions 1 and 2. APS rather than PAPS is the form

TABLE 3: The Enzymes of Respiratory Sulfate Reduction

1. ATP:sulfurylase

$$\text{ATP} + \text{SO}_4^{2-} \rightarrow \text{APS} + \text{PP}_i \quad (28)$$
2. Inorganic pyrophosphatase

$$\text{PP}_i + \text{H}_2\text{O} \rightarrow 2\text{P}_i \quad (28)$$
3. APS:reductase

$$\text{APS} + 2e \rightarrow \text{AMP} + \text{SO}_3^{2-} \quad (20)$$
4. Bisulfite reductase

$$\text{HSO}_3^{-1} + 2e + 3\text{H}^{+} \rightarrow \text{S}_3\text{O}_6^{2-} + 3\text{H}_2\text{O} \quad (11)$$
5. Trithionate reductase

$$\text{S}_3\text{O}_6^{2-} + 2e \rightarrow \text{S}_2\text{O}_3^{2-} + \text{SO}_3^{2-} \quad (10)$$
6. Thiosulfate reductase

$$\text{S}_2\text{O}_6^{2-} + 2e + \text{S}^{-2} + \text{SO}_3^{2-} \quad (8)$$

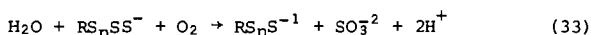
in which SO_4^{2-} is reduced to SO_3^{2-} with the formation of AMP, Table 3, reaction 3, by APS reductase in a reversible oxidation-reduction reaction. Sulfite (or bisulfite) is not directly reduced to S^{-2} by a single enzyme as in the biosynthetic pathway but rather three separate reductive steps are involved. In a complex reaction involving

three molecules of sulfite, SO_3^{2-} is reduced to trithionate ($\text{S}_3\text{O}_6^{2-}$) by a hemoprotein, bisulfite reductase, of which there are three different types, desulfoviridin, desulfurubidin (12) and P582 (1), Table 3, reaction 4. Trithionate is next reduced to thiosulfate with the concomitant formation of sulfite by trithionate reductase, Table 3, reaction 5. The thiosulfate is then reductively cleaved to yield S^{-2} and a second molecule of SO_3^{2-} , Table 3, reaction 6. The electron donors for these reductions have not been definitively established but they appear to be low-molecular weight electron transfer proteins. In both pathways, the result is identical in that SO_4^{2-} is reduced to S^{-2} ; however, the respiratory pathway requires one less ATP and four discrete reductive steps rather than the two involved in the biosynthetic pathway. These differences probably reflect the different physiological roles of the pathways.

The respiratory pathways involved in the oxidation of reduced sulfur compounds to SO_4^{2-} are less well defined than those in the reduction of sulfate. The key reaction is the oxidation of a cofactor or enzyme-bound polysulfide (15) to sulfite in an oxygen requiring oxidation, Table 4, reaction 1 (33). Elemental sulfur and

TABLE 4: The Reactions of Respiratory Sulfur Oxidation

1. Polysulfide oxidase



2. Thiosulfate formation



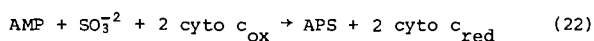
3. Thiosulfate reductase



4. Sulfite oxidase



5. APS reductase



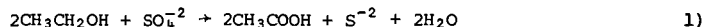
6. ADP sulfurylase



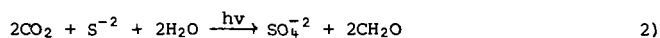
sulfide can form this "bound polysulfide" (R) and thus enter the reaction sequence; however, little is known about the details of these interactions. Sulfite is a highly reactive molecule and non-enzymatically combines with elemental sulfur to form thiosulfate, Table 4, reaction 2. Thiosulfate is returned to the main respiratory pathway by reductive cleavage to sulfide and sulfite by thiosulfate reductase, Table 4, reaction 3. The final step is the oxidation of SO_3^{2-} to SO_4^{2-} and is accomplished by two enzymatic pathways. The first is the simple oxidation of SO_3^{2-} to SO_4^{2-} by the enzyme, sulfite oxidase, in certain of the *Thiobacilli*, Table 4, reaction 4. This oxidase has been reported to be absent in the photosynthetic bacteria (36). The second pathway, found in the photosynthetic bacteria and some of the *Thiobacilli*, involves the oxidation of SO_3^{2-} in the presence of AMP to the level of sulfate as APS by APS reductase, Table 4, reaction 5. The high energy sulfate can then be exchanged for a phosphate group to yield ADP by the enzyme, ADP:sulfurylase to produce biologically utilizable energy, Table 4, reaction 6. Thus, microorganisms utilizing the APS pathway are able to obtain energy by means of a substrate phosphorylation in addition to either oxidative phosphorylation or photophosphorylation. In all considerations of the biological sulfur cycle, it must be borne in mind that the

oxidation of reduced sulfur compounds yields energy and that the reduction of sulfate requires energy although the reduction of sulfate can be coupled with an oxidative reaction which produces more energy than the reduction of SO_4^{2-} requires and thereby produce energy for growth.

An important aspect of the biological sulfur cycle is the ability of certain of these anaerobic microorganisms to link and thereby modify their fermentative respiratory pathways by means of the intracellular transport or transfer of molecular hydrogen. This linking of fermentations allows these anaerobic bacteria to grow under some unexpected and surprising conditions in an almost symbiotic relationship. There are now several well documented examples of this biological phenomenon. Methanobacillus omelianskii has been demonstrated to be a mixed culture growing in this type of relationship and forming acetate and CH_4 from CO_2 and ethanol (3). One of the organisms, the S organism, oxidizes ethanol to acetate and H_2 but grows poorly. The second organism, the H organism, reduces CO_2 to CH_4 with H_2 and appears to "pull" the oxidation of ethanol to acetate by the oxidation of H_2 as growth is greater in the mixture than in pure culture (26). Chloropseudomonas ethylica has been demonstrated to be a mixed culture which photosynthetically oxidizes ethanol to acetate (7). The culture consists of a sulfate-reducing bacterium which oxidizes ethanol to acetate with the reduction of SO_4^{2-} to S^{2-} as shown in Eq. 1.



and a green sulfur bacterium which photosynthetically oxidizes S^{2-} to SO_4^{2-} as shown in Eq. 2.

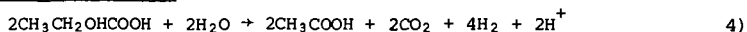


The possible involvement of intercellular H_2 transfer in this relationship has not yet been resolved. A third example involves an obligatory relationship between a sulfate-reducing bacterium and a methanogenic bacterium. Sulfate (or fumarate) is obligatory for the growth of species of Desulfovibrio on lactate as shown in Eq. 3.



Recently, it has been demonstrated that the sulfate-reducing bacteria can oxidize lactate to ethanol when grown in the presence of methanogenic bacteria and the electrons (as H_2) utilized for the reduction of CO_2 to CH_4 rather than the reduction of SO_4^{2-} to S^{2-} (2). This relationship involving intercellular H_2 transfer is shown in Eqs. 4, 5 and 6.

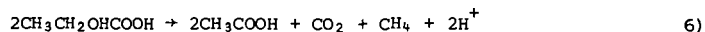
Sulfate reducing bacterium



Methanogenic bacterium



Sum:



In essence, CO_2 is functioning as electron acceptor for the fermentation of lactate (and probably other electron donors) and H_2 is transferred between these two anaerobic but physiologically different types of bacteria. The mechanism of this relationship has been postulated to be the "pulling" of lactate oxidation by the utilization of H_2 for CH_4 formation. This concept is also supported by the observation that hydrogenase is concentrated around the outside of the sulfate-reducing bacteria. Thus,

methane formation is operating as an "electron sink" or terminal oxidase and could conceivably be "pulling" the complex series of fermentative reactions occurring in the cellulose breakdown.

The observations offer a new theoretical basis for the interpretation of a portion of the microbiology and biochemistry in anaerobic sediments of fresh and marine waters. Intercellular H_2 transfer appears to be a specific adaptation of anaerobic bacteria which allows them to greatly extend their growth potential. Thus, the number of physiological types of microorganisms involved in the transformation of organic materials may be far fewer than previously anticipated. The ideas also suggest that a specific environment may have unexpected potential for microbial activities such as sulfate reduction, hydrogen utilization or nitrate reduction. It has also recently been established that anaerobic sediments are stable enough so that classical biochemical and physiological experiments can be performed with sediments by treating them as bacterial cultures (5). Investigations utilizing these two concepts should lead to a much greater understanding of the reactions occurring in organic deposits and indicate the ways in which these complex fermentations can be applied to specific problems of economic concern.

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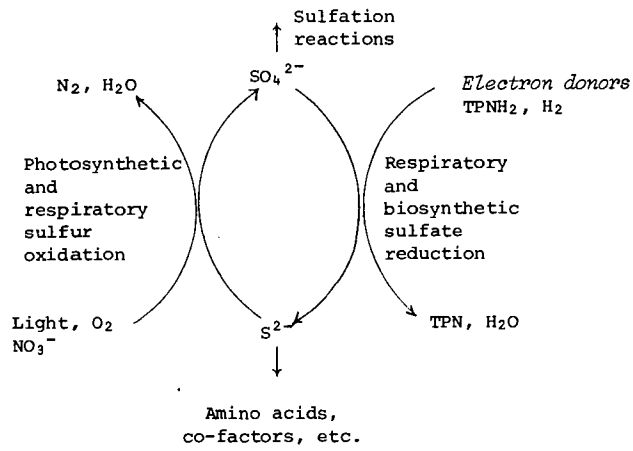


Fig. 1. A simple representation of the biological sulfur cycle.

THE GENESIS AND STABILITY OF NITROGEN IN PEAT AND COAL

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Coal consists of the fossilized remains of bog and swamp-shore vegetation, which, following diagenesis, was preserved by water and modified by heat and pressure. Geochemists generally accept as valid the concept of a coalification series: vegetation-peat-brown coal-lignite-bituminous coal-anthracite.

Coal commonly contains 1-2% N in fixed forms which are highly resistant to biodegradation. The woody tissues of the originating vegetation--predominately tree-ferns--probably averaged about 1% N, which was of a biodegradable nature. Assuming them to be similar in structure to present-day woody tissues, about 20% of tree-fern cells contained proteinaceous material. Humic substances derived from woody and more succulent tissues as a result of microbial activities and oxidative polymerization reactions probably contained 2-5% N, although the average N content of the peat resulting from plant tissue deposition and decay remained at about 1%. The N content of bituminous coal generally is slightly higher than that of peat and lignite--about 1.5 to 1.75%--but decreases to less than 1% in anthracite.

The C/N ratio typically increases from about 50/1 in wood to 65/1 in peat and lignite. However, the C/N ratio decreases in low-rank bituminous coals, then increases with increase in rank (55/1 in high-rank bituminous coals to 100/1 or greater in anthracite). It is evident that N was gained relative to C (or C was lost) during the latter stages of diagenesis.

The accretion of N by peat may continue after its formation and subsequent submergence in waters through deposition of microbial (microflora and microfauna) protein. The total amino acid content of peat is considerably higher than in the original plant material; at least 5-10% of peat organic matter is considered to be derived from microbial tissue (1). For example, the weight of bacterial tissue per acre foot of peat might range between 35-700 pounds at any given time, corresponding to about 5-115 pounds of N. This range is calculated by assuming 35-700 million bacteria per gram of moist peat (2, 3), a volume of 1 cubic micron per organism, and a cell density of 1.04. Soil bacteria usually outnumber actinomycetes by 10:1, and fungi by 100:1, but the weight of bacteria is about equal to and half that of the actinomycetes and fungi, respectively. As can be seen, the total living and newly deceased biomass in peat could be substantial. Obviously, N accretion through deposition of microbial tissue implies the presence of sufficient fixed N to sustain microbial growth. Such N could be obtained from *in situ* biological fixation of atmospheric N₂ or from the transport of fixed N in sediments and aquatic life to peat beds.

Determining how and in what forms the N was preserved may be more instructive in understanding the genesis of N in coal than speculating on the primary sources of N in a coalification series. The time, manner, and circumstances of nitrogen accretion during or shortly after diagenesis is of lesser importance if one accepts the concept of a coalification series progressing from peat to anthracite rather than the concept advanced by Fuchs (4), which holds that lignites are formed under aerobic conditions and bituminous and anthracite coals are formed under anaerobiosis. More importantly, a question central to understanding the presence of fixed N in coal is how nitrogenous products of microbial activity acquire stability against further microbial and chemical decomposition over geological times.

SOIL HUMUS FORMATION

Humus, as used here, refers to the debris of higher plants, microflora, and microfauna in various stages of biochemical and chemical alteration. Early work on soil humus formation was much influenced by chemical studies of humus in peats and coals. Granting that the factors influencing humus formation in soils, marshes, peat bogs, etc., may be very different, one nevertheless may be justified in seeking common mechanisms for humus formation under widely different conditions because of the known gross similarities of certain humic substances (alkali-extractable, acid-precipitable substances) in soils and in lake and marine sediments.

Recent N tracer (^{15}N) studies support the postulate of Jansson (5) that there exists in soil a large pool of relatively passive organic N, all or part of which is in equilibrium with a much smaller pool of labile organic N. Usually, when N is added to soil, some becomes immobilized through microbial activity, entering first a pool of labile organic matter, then being redistributed among progressively more refractory, bioresistant substances in the passive pool (6-10). Current knowledge of the organic forms of N in these pools is based largely on the chemical analysis of organic N compounds released by hydrolysis of soils with hot acids [for reviews, see Bremner (11, 12)]. Such hydrolysis studies indicate that the labile organic N pool consists largely of bound amino acids and amino sugars (mainly glucosamine and galactosamine), existing perhaps as mucopeptides (amino acid--amino sugar complexes), teichoic acids (ester-linked alanine-organophosphate polymers), and chitinous substances. Amino acids and hexosamines normally comprise 20-50% and 5-10%, respectively, of the total organic N of soils. Purines, pyrimidines, ethanolamine, and other N compounds also have been identified in soils, but the chemical nature of about half of soil organic N is not well understood. It is this unidentified, relatively stable fraction that is of geochemical interest.

In soils, peat bogs, and like environments, labile forms of N are assimilated by microorganisms. The microorganisms die and decay, the tissues of one generation being food for succeeding ones. With each cycle of generation and decay, waste products of metabolism are released to the microenvironment. Ammonium N and amino acids can be considered

such wastes. As long as these waste products re-enter vital processes, and then recycle as part of new living tissue, there is no mechanism for acquiring stability. However, the recycling processes may be interrupted by chemically binding labile nitrogenous substances to other intracellular or extracellular constituents to form biochemically resistant and chemically inert materials, or by decreasing their physical accessibility to enzymatic and nonenzymatic attack.

The "physical inaccessibility" concept is supported by the finding that destruction of physically stable microaggregates in soil consisting of clay mineral-organic matter complexes renders the organic matter more susceptible to chemical and microbial attack (13). Also, the entrapment of ammonia within clay lattices is another protective mechanism for soil N. Clay-protected N could survive the coalification processes and appear in coal as part of clay mineral contaminants in low-rank coals.

Much work has been reported in support of the view that stable N complexes in soil are produced by reactions of lignin- and cellulose-derived phenols or quinones with amino acids [e.g., see (11-20)] and the reactions of oxidized lignins with ammonia (21). The dark-colored substances produced by such reactions have chemical properties similar to the humic substances found in soils, peats, and sediments. A detailed analysis of the extensive work on the role of lignin in humification processes is beyond the scope of this paper.

Chemical fractions of humic substances (e.g., humic, fulvic, and hymatomelonic acids) are probably not simple chemical entities, but more likely are mixtures of components of heterogeneous structure. They are noncrystalline, which suggests that they are not formed through enzymatic activity. Although the dark humic substances exhibit the properties of oxidized lignins, it is reasonable to assume that lignins must be drastically altered before entering oxidative polymerization or polycondensation reactions with ammonia and amino acids (22, 23). Natural and unaltered lignins are too chemically inert to form complex, biologically stable polymers with amino acids. Also, formation of such polymers extracellularly in soil from lignin residues may not be extensive because only small amounts of lignin degradation products are found in soils and peats. For example, alkaline-nitrobenzene oxidation of soil organic matter yielded syringyl, guaiacyl, and p-hydroxyphenyl residues amounting to less than 1% of the total soil C; for peat, the yield was 1 to 4% (24).

The proximity of reactants to each other, their concentrations, the reaction site microenvironment, and the time that each reactant is released to the microenvironment are factors which may determine the extent of formation of dark humic substances and their nature. These factors themselves are influenced by the type of vegetation undergoing diagenesis (e.g., woody tissues are characterized by relatively high protein and lignin contents as compared to sphagnum moss). As plant tissue decays, loosely bound proteins and carbohydrates are attacked first, followed by peptides and methylated polysaccharides. Lignins are relatively resistant to biodegradation. It appears, therefore, that

ammonia and amino acids would be released from plant residues to the soil at a particular microsite, and then transformed or assimilated before lignin- or cellulose-derived phenols and quinones are produced at the microsite. Even though amino acids may persist unmodified in soils for many years, there is evidence that a considerable portion of soil amino acids is not bound to lignin (11) and may form stable complexes with transition series metals (25).

The intact cell is a potential reaction chamber in which chemically active substances may be intimately associated at high concentrations in a microenvironment favorable for reaction. Recently, considerable attention has been given to the possibility that humic substances are formed by autolysis of microorganisms (23). The presumption that stable organic N polymers can be formed intracellularly is supported by evidence that dark humic substances are formed by chemical reactions of biochemically produced reactants, that the sequence of reactant production in soil may not be conducive to extensive extracellular formation of humic substances, and that the dark humic substances formed in different media and at different geological times are similar.

POSSIBLE INTRACELLULAR FORMATION OF HUMIC SUBSTANCES

Living cells contain the enzymes needed for degrading their autogenous substances (e.g., proteins, peptides, and cellulose) and for the further reaction of the degradation products (e.g., the oxidation of phenols to quinones and polyphenols by phenolases). However, ligninase has not been isolated from higher plant or microbial tissue, notwithstanding the specific evidence of ligninase activity in fungal cells. In woody cells, lignin is deposited in the interstices between the micellar strands and microfibrils of cellulose and other microcrystalline components of the cell wall. After the cell or tissue dies, removal of the lignin leaves the cell wall morphologically intact. Within the protection of a relatively bioresistant cell wall, high concentrations of monomeric substances can accumulate as autolysis proceeds.

Quinones can condense with α -amino acids through the amino group, leaving the acidic carboxyl groups free. Cross-linking with adjacent quinones could occur through diamino-amino acids (e.g., lysine) or thiol-containing amino acids (e.g., cysteine). Polycondensation would result from intermolecular interactions between compounds possessing at least two functional groups capable of esterification. The order and pattern of polycondensation would be irregular, resulting in a 3-dimensional amorphous substance (a heteropolycondensate co-polymer with side chains) composed of many phenolic-quinolic-amino acid units. It has been postulated that such polymeric substances, by virtue of their isolated resonance groups, would absorb light of all wavelengths and appear dark in color, be soluble in alkalis because of their free carboxyls, be slightly soluble in organic solvents because of their predominantly condensed aromatic nature, and be precipitated from alkaline solution by acids and heavy metals (26). Such co-polymers would be resistant to chemical and microbial attack because of their high molecular weight, their cross-linked, covalent bonding, and their heterogeneous, predominately nonlinear structure of nonrepeating units.

The humic substances formed within the cell would be released by extracellular microbial and chemical attack on the cell wall. Since their overall mode of formation is similar, dark humic substances found in different environments (e.g., soils, peats, and sediments) would be expected to have similar gross properties. In time, and depending on environmental factors, the linear side chains of the large, irregularly spherical co-polymer would be degraded, leaving a substance that would require the fortuitous, unlikely association of several enzymes to effect its further degradation.

NITROGEN FORMS IN COAL

Little is known with certainty about the N forms in coal and it appears premature to speculate about the metamorphic conversion of humic substances whose structures are only grossly identified. There is evidence that N occurs largely as heterocyclic structures (27, 28), such as nicotinic acid (29). A presumptive analysis of coal extracts after physical and chemical treatment yielded the following hypothetical distribution of nitrogen structures: Water phase--purine bases and structures with urea, amino acid, and peptide units (35%), carbazole structures yielding ammonia (10%), low-molecular weight cyclic bases and phenylamines (3%); Chloroform phase--hydrophilic bases, nonbasic N compounds, and fatty amines (23%); Residual coal--high-molecular weight N compounds (3%). Upon pyrolysis, 26% of the N compounds yielded N_2 (30).

Among the amino acids found in peat were glycine, aspartic and glutamic acids, alanine, leucine, threonine, and valine (31). Monoamino and diamino acids have been identified in peat, lignite, and subbituminous coal, but no diamino acids have been found in bituminous and anthracite coals (28). Glycine and aspartic and glutamic acids were found in hydrolysates of anthracite estimated to be over 200 million years old (32).

Free porphyrins have been identified in polar solvent (e.g., ether or pyridine) extracts of bituminous coal (33). Metal-porphyrin complexes may be present in concentrations as high as 7000 ppm, about 100 times those of free porphyrins. Nickel and vanadium complexes are especially stable. Porphyrins in coal originate in the chlorophyll and respiratory pigments of green plant tissue and have been preserved in water-logged peat because of their greater stability in anaerobic biological environments. Their presence lends support to the hypothesis that pressure and moderate heat are the agents of peat metamorphosis because porphyrin stability increases with pressure and decreases with heat. Also, studies of porphyrins in bitumens give support to the hypothesis that petroleum is formed in brackish environments from asphaltic constituents resulting from the alteration of marine and terrestrial plant and animal organic matter (34).

TRACER STUDIES

Use of the N tracer, ^{15}N , has contributed greatly to an understanding of the turnover of N in biological mineralization-immobilization reactions, processes which proceed simultaneously and in opposite directions [for an extensive bibliography, see Hauck and Bystrom, (35)]. However, N tracer techniques have not been used effectively to clarify the chemical nature of humic materials, largely because experiments have not been devised to make maximum use of ^{15}N for this purpose. It would be instructive to follow the detailed, sequential decay of higher plant and microbial tissue labeled with ^{13}C and ^{15}N , and to attempt to isolate labeled polycondensation products from cell populations in various stages of autolysis. Comparisons should be made of the distribution of tracers in different humic fractions, as affected by the precursor tissue. For example, woody tissue may produce more highly aromatic, humic substances, such as those found in coals, while the corresponding humic fraction from proteinaceous tissue may be more aliphatic in character. However, such comparisons might be valid only if care is taken to separate extracellular from intracellular formation of humic substances, should such a distinction exist.

Carbon isotope studies show no correlation between isotopic composition, degree of coalification, and geological age of coals (36). From this one may infer that the C in coal was derived largely from land plants which absorbed carbon dioxide of uniform C isotopic composition and that no measurable C isotope fractionation occurred during diagenesis.

Slight but significant variations have been observed in the N isotopic composition of different peats and coals (37-39). The N in coal tends to have a slightly higher ^{15}N concentration than vegetation in the vicinity of the coal seam (38), but definite conclusions are not justified from the limited data available. In another study (39) C isotope analyses indicate that some Dutch natural gas deposits originated from recoalification of coal seams 3000 and 5000 meters below sea level. Nitrogen in gases obtained from these deposits was enriched in ^{15}N , while ammonia obtained from the coal (coke-oven gas) was depleted in ^{15}N (relative to atmospheric N_2), leading to the speculation that the N in natural gases was not derived from the coal. Measurements of N isotope ratios in natural gases have also been used to explain the parallel increase in He and N_2 in gases with increase in age of reservoir rock (40) and to elucidate the origin of N in gases associated with crude oils and sedimentary materials (41).

The limited number and scope of the studies referred to above make it difficult to assess whether further studies of this kind will prove useful in clarifying the genesis of coal, kerogen, petroleum, and natural gases. Obviously, if the N isotope ratio of N occluded in methane, for example, is similar to but slightly lower than that of a nearby deposit of organic material, then one has reason to assume that the methane was derived from that deposit. Also, a slightly lower N isotope ratio for N in methane suggests the occurrence of isotope fractionation as C-N bonds are ruptured during gas formation.

There is a time gap of about 200 million years separating current studies of humification processes and the events which converted vegetation to coal. Because the isotope ratio reflects the cumulative effects of nitrogen cycle processes, in-depth studies of the N isotopic composition of peats, coals, and their associated materials may prove helpful in separating events that occurred during different geological times.

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INTRODUCTION

Sulfur is a necessary element for the sustenance of all living systems. It is therefore not at all surprising that sulfur is found in abundance in coal, a rock composed primarily of organic detritus.

The forms of sulfur in coal as reported by chemical analyses (ASTM 1974) are: organic sulfur, pyritic or sulfide sulfur, and sulfate sulfur. The last two are inorganically combined within the coal and will be discussed here. Other analytical techniques have been used to identify native or elemental sulfur in coals (Yurovski, 1940; Berteloot, 1947) and also in modern peats (Casagrande, *in* Spackman et al., 1974, p. 63, 219). The amounts of elemental sulfur that have been reported are small and would not be significant in coal utilization.

Sulfate sulfur is also generally of only minor importance in fresh coal samples and except in rare instances occurs in significant amounts only as the coals oxidize (weather). Organic and pyritic sulfur comprise essentially all of the sulfur found in most coals. Yancey and Geer (1968) list analyses of these two forms of sulfur in various coals of the world and these range from a low of 0.44 percent to a high of 9.01 percent total sulfur. Only rarely would one expect to find coals in which the percentage of sulfur would not be included in that range. The organic sulfur content of the coals listed by Yancey and Geer ranged from 11.4 percent to 97.1 percent of the total sulfur. Gluskoter and Simon (1968) reported a mean value of 1.56 for the ratio of pyritic to organic sulfur in 473 face-channel samples of Illinois coals.

SULFUR BEARING MINERALS IN COAL

Iron Sulfides—Pyrite is the dominant sulfide mineral found in coals. Marcasite has also been found in many coals and may be the dominant form in some coals of lower rank (Kemežys and Taylor, 1964). Pyrite and marcasite are dimorphs, minerals that are identical in chemical composition but differ in crystalline form. Pyrite is cubic and marcasite is orthorhombic. The two minerals cannot generally be differentiated in coals except by determining their crystalline structures, usually by X-ray diffraction methods. The term "pyrite" is often used to refer to the undifferentiated iron disulfide minerals in coals.

Rather extreme variations in morphology, size, and mode of occurrence characterize the iron sulfide minerals in coals. These variations arise because of the different geochemical environments in which the minerals were formed and the time of their genesis. Some sulfides were formed contemporaneously with the coal in a peat swamp and are therefore syngenetic. The syngenetic pyrite includes sub-micrometer-sized particles and also some nodules with diameters as large as a meter. These syngenetic sulfides are the response to the geochemical environment during or immediately following the peat formation, which was approximately 300 million years ago for the coals of carboniferous age. Other of the sulfides are epigenetic; they formed within the coal seam subsequent to the first stages of coalification. The most common form of epigenetic iron sulfide in coal is pyrite deposited along vertical fractures (cleat). I am not aware of any report of marcasite as an epigenetic mineral in bituminous coals of North America, but a mixed marcasite-pyrite cleat filling in a subbituminous coal from Wyoming is shown in Plate 1. Other epigenetic and syngenetic sulfides are shown in scanning electron photomicrographs in Plate 1.

Other Sulfide Minerals—A number of sulfide minerals other than iron sulfides have been reported in coals, including galena (PbS), chalcopyrite (CuFeS₂), arsenopyrite (FeAsS), and sphalerite (ZnS). These generally occur only in small amounts. However, coals from northwestern Illinois that contain as much as 5350 ppm zinc and up to 1 percent sphalerite have recently been described by Ruch et al. (1974) and Miller (1974). The sphalerite occurs as a cleat filling up to 10 mm in width (Plate 2).

Sulfate Minerals—Gypsum (CaSO₄·2H₂O) and barite (BaSO₄) have both been identified as cleat-filling minerals or in nodules in unweathered coals (Plate 2). However, their occurrences are rare and sulfate minerals do not generally comprise a significant portion of the total sulfur in coal.

Because pyrite and marcasite oxidize rapidly when exposed to moist air, a number of different phases of ferrous and ferric sulfates may form. The following have been identified as oxidation products of iron sulfides in Illinois coals (Gluskoter and Simon, 1968): Szomolnokite (FeSO₄·H₂O), rozenite (FeSO₄·4H₂O), melanterite (FeSO₄·7H₂O), coquimbite (Fe₂(SO₄)₃·9H₂O), roemerite (FeSO₄·Fe₂(SO₄)₃·12H₂O), and natrojarosite ((Na₂K)Fe₃(SO₄)₂(OH)₆). Although these are not present in fresh coals they can become abundant in weathered, oxidized coal samples. The amount of sulfate sulfur reported in the chemical analyses of many coals is a function of the length of time since the fresh sample was collected and of the manner in which it was sorted. Several iron sulfates are shown in Plate 2.

ACKNOWLEDGEMENTS

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ILLUSTRATIONS

Plate 1. Pyrite in Coals: Scanning Electron Photomicrographs

- A. Framboids in low-temperature ash of a sample from the DeKoven Coal Member (bituminous), southern Illinois
- B. Octahedra in low-temperature ash of a sample from the DeKoven Coal Member (bituminous), southern Illinois
- C. Epigenetic cleat filling in a sample of the Opdyke Coal Member (bituminous), southern Illinois
- D. Cast of plant cells from the low-temperature ash of a sample from the Colchester (No. 2) Coal Member (bituminous), northern Illinois
- E. Epigenetic pyrite along inclined shear surface in a sample of lignite, North Dakota
- F. Epigenetic cleat filling in a sample from the Colchester (No. 2) Coal Member (bituminous), northern Illinois

Plate 2. Sulfide and Sulfate Minerals in Coals: Scanning Electron Photomicrographs

- A. Marcasite, epigenetic, along cleat in a sample from a sub-bituminous coal, Wyoming
- B. Sphalerite (ZnS), along cleat in a sample from the Herrin (No. 6) Coal Member (bituminous), northwestern Illinois
- C. Barite (BaSO_4) with marcasite and pyrite in a sample from a sub-bituminous coal, Wyoming
- D, E, and F. Iron sulfates which formed on bituminous coal samples subsequent to their having been collected from fresh exposures. X-ray diffraction analyses of these samples identified melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and coquimbite ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$).

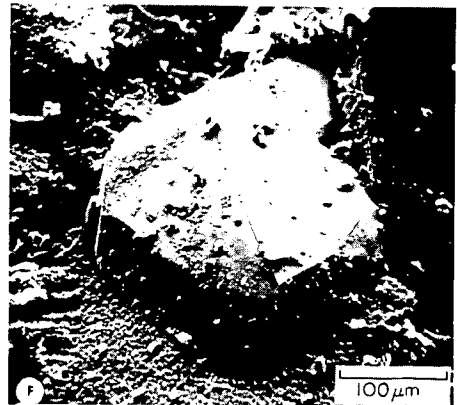
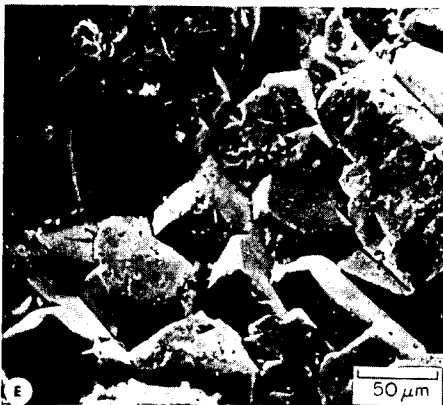
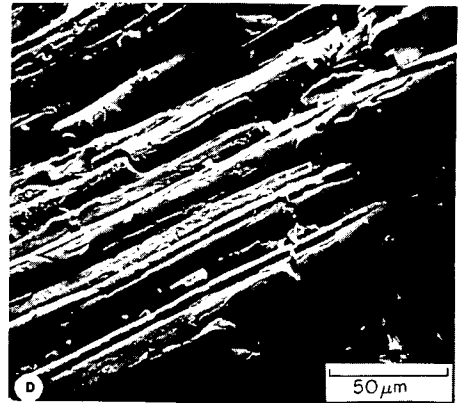
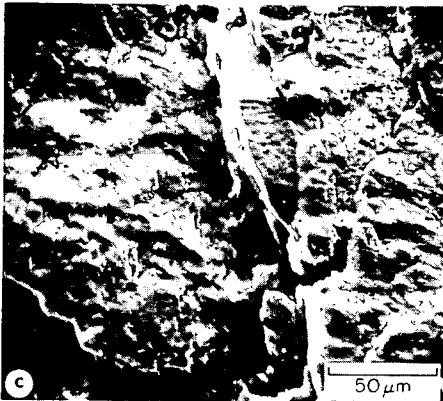
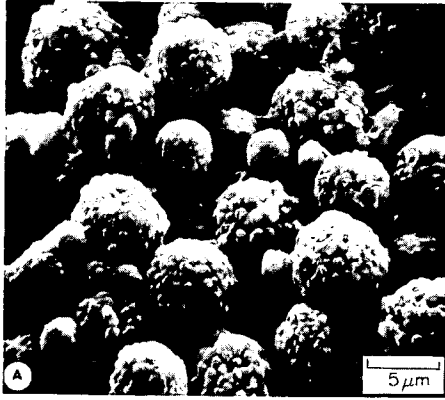


Plate 1. Pyrite in Coals

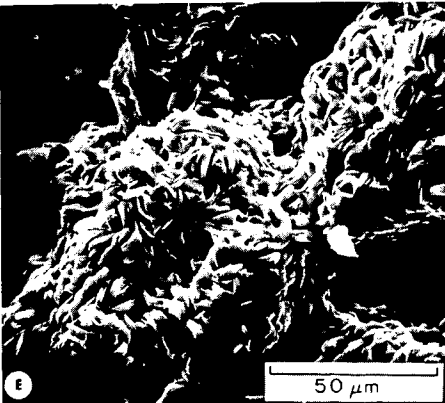
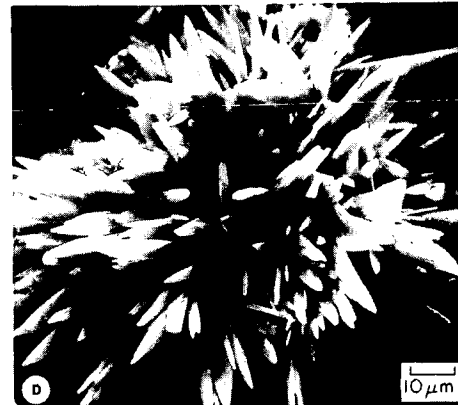
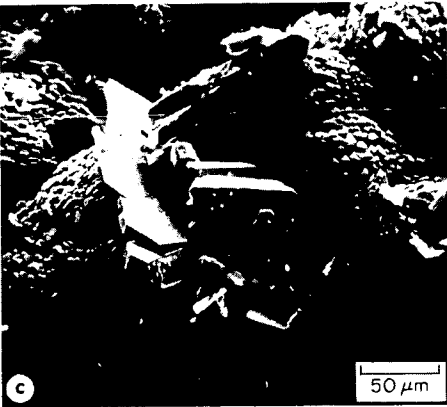
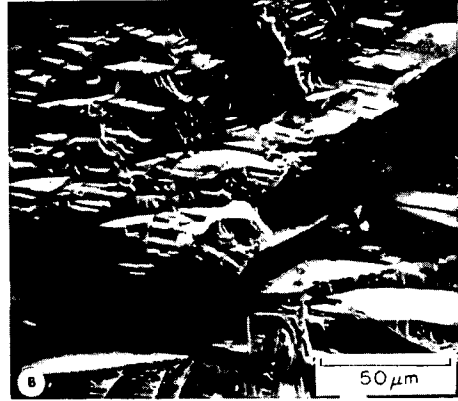
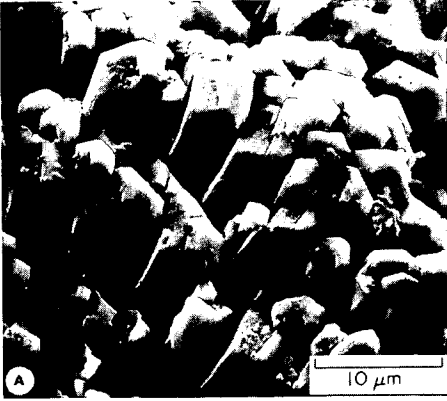


Plate 2. Sulfide and Sulfate Minerals in Coals

Determination of Forms of Sulfur in Coal

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INTRODUCTION

The need for low-sulfur coal has assumed major proportions. Shortages of other fossil fuels, restrictions on sulfur oxide emissions, and technical problems associated with the use of high-sulfur coals in newly proposed coal conversion processes are contributing to the crisis. It is now apparent not only to coal specialists but also to others that the emission standards and technical problems associated with high sulfur content of bituminous coals are contributing greatly to the severity of the fuel shortages in the United States. Consequently, it is appropriate to discuss old and new methods of evaluating the sulfur status of coal and to reexamine some of the problems associated with their application.

Free sulfur as such does not occur in coal to any significant extent. Sulfur is present in coal in organically bound combinations, in inorganic compounds mainly as pyrite (FeS_2), and especially in weathered coals as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and as ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). In a few coals, significant amounts of other inorganic sulfates and sulfides, e.g. barite (BaSO_4) and sphalerite (ZnS), (1,2) which normally occur only in trace concentrations, may be present.

The three forms of sulfur commonly measured in coal are sulfate, pyritic, and organic. Although less frequently determined than total sulfur, they are, perhaps, the most significant in terms of coal utilization. Of the two predominant sulfur forms, pyritic and organic, the former can be partially removed by conventional gravity coal cleaning procedures prior to combustion, but the latter cannot. The amount of pyritic sulfur in Illinois coals and the percentages of it that can be removed with reasonable coal recovery (80%) were recently reported by Helfinstine et al. (3,4). For 64 coals, they found that the total sulfur removed as pyrite in laboratory washing studies varied from about 10 to 65%. The pyritic sulfur that was removed with 80% coal recovery varied from about 10 to 90% and averaged about 60%.

Although significant amounts of pyritic sulfur can usually be removed by physical means, very finely divided or framboidal pyrite is not amenable to reduction by such treatment. For complete removal of pyritic sulfur, a combination of physical and chemical extraction methods is usually required. Methods of this type are currently being developed, but these have not been employed on an industrial scale (5).

Similar methods for the reduction of organic sulfur, without destruction of the coal molecule itself, have not been developed. Even if 100% of the pyritic sulfur were removed from all the Illinois coals produced, only about 15% would meet current environmental standards without supplementary controls (3,4).

Because the degree to which sulfur can be reduced in coal is primarily a function of the forms of sulfur contained in the coal, analytical methods for their accurate determination are essential.

ASTM FORMS OF SULFUR INVESTIGATION

Committee D-5 on Coal and Coke, of the American Society for Testing and Materials (ASTM), began a study of methods for the determination of forms of sulfur in coal in 1957. This study eventually led to the current Standard Method D-2492,

Forms of Sulfur in Coal (6). In this procedure, total sulfur and only two of its three forms - sulfate and pyritic - are determined. The third form, organic sulfur, is calculated by difference:

$$\text{Organic S} = \text{Total S} - (\text{sulfate S} + \text{pyritic S}).$$

For this method, it is not only essential to obtain accurate values for sulfate and pyritic sulfur forms, it is also necessary to obtain accurate total sulfur values. Any errors made in total, pyritic, or sulfate sulfur determinations will be cumulative in the organic sulfur calculation. Unfortunately, there are no published methods for the direct determination of organic sulfur that will permit the sum of independently determined values for the three forms of sulfur to be checked against an independently determined total sulfur value. This has led to a number of problems, which will be discussed in more detail later.

A flow sheet for ASTM Standard Method D-2492, Forms of Sulfur in Coal, is given in Figure 1. The method is based on the different solubilities of sulfate and pyritic sulfur in HCl and HNO₃. Sulfate sulfur is soluble in dilute HCl, both sulfate and pyritic forms of sulfur are soluble in HNO₃, and organic sulfur is insoluble in the acids. Pyritic sulfur is generally determined by extracting the coal residue from the sulfate sulfur determination (Figure 1), although it may also be determined on a separate coal sample if corrections for the sulfate sulfur or iron are made. Pyrite is oxidized by HNO₃ to ferric iron and sulfate, but it is the ferric iron associated with the pyrite that is usually determined rather than the sulfur (Figure 1). The HNO₃ extraction may oxidize small amounts of organic matter that contains sulfur. This would be erroneously determined as part of the pyritic sulfur. Organic sulfur is calculated by difference as previously described.

During the ASTM round-robin testing of this method, large amounts of data were generated and subsequently compiled by Krumin (7,8,9,10) for Committee D-5. The results and conclusions of this study are unavailable in published form, but a brief summary of its nature and the conclusions drawn are as follows*.

1) Five coal samples containing from 1.6 to 24% sulfur, each ground to pass a -60 mesh and -200 mesh-sieve, and analyzed by five different laboratories gave essentially the same results for forms of sulfur. Thus, the use of -60 mesh coal was recommended.

2) Further studies using methods originally developed by Powell and Parr (11) and Powell (12) were conducted by 24 laboratories, each analyzing two coals in triplicate and using the coal extraction and method variations given in Table I. In all cases, organic sulfur was determined by differences. Results of this study are summarized in Table I. Table II presents the results of the t-test of means, and Table III presents results of the F-test of variances as performed on the data determined by the various methods for sulfate and pyritic sulfur in coal samples designated S-1 and S-2. Conclusions were drawn by Krumin (10) and presented at the meeting of ASTM Committee D-5, January 30, 1961:

Total Sulfur-Eschka Method (ASTM D-3177). Deviations in the data reported by the various laboratories were within, or exceeded by only a small amount (0.01 to 0.05%), ASTM limits for maximum deviations of results.

Sulfate Sulfur (ASTM D-2492). The results determined by the two methods Sulfate Sulfur, Short Extraction and Sulfate Sulfur, Long Extraction are in close agreement, and are characterized by almost identical values for the standard deviation, repeatability and reproducibility. The great advantages of the 30-minute extraction procedure over the 40-hour technique make the method Sulfate Sulfur, Short Extraction the more suitable method for use in the routine analysis of coal.

* Permission to summarize this work was granted by the Executive Committee of ASTM Committee D-5 on Coal and Coke.

TABLE I. STATISTICAL EVALUATION*

Experimental procedure	Sample	Meant data (%)	Standard deviation	Repeat-ability	Reproduc-ibility
Total Sulfur	S-1	2.93	0.0945	0.0610	0.2514
	S-2	2.94	0.0846	0.0928	0.2142
Sulfate Sulfur,	S-1	0.08	0.0131	0.0196	0.0311
HCl Short Extraction (30 min.)	S-2	0.16	0.0124	0.0214	0.0322
Sulfate Sulfur	S-1	0.08	0.0115	0.0196	0.0339
HCl Long Extraction (40 hrs., 60° C)	S-2	0.15	0.0124	0.0191	0.0316
Pyritic Sulfur, Short	S-1	1.75	0.1799	0.1412	0.4412
HNO ₃ Extraction (reflux, 30 min.), Gravimetric Determination	S-2	1.62	0.1637	0.14555	0.4069
Pyritic Sulfur, Long	S-1	1.74	0.1952	0.1614	0.5085
HNO ₃ Extraction (24 hrs., room temp.), Gravimetric Determination	S-2	1.59	0.1228	0.1460	0.3359
Pyritic Sulfur, Short	S-1	1.74	0.1553	0.1198	0.4119
HNO ₃ Extraction (reflux, 30 min.), Titrimetric Determination of Iron	S-2	1.58	0.0943	0.1213	0.2516
Pyritic Sulfur, Long	S-1	1.85	0.1027	0.0922	0.2815
HNO ₃ Extraction (24 hrs., room temp.), Titrimetric Determination of Iron	S-2	1.59	0.0974	0.0998	0.2553

*After a thesis by E. Fasig, Jr., Engineering and Experiment Station, Ohio State University, Columbus, OH.

†Moisture-free.

TABLE II. RESULTS OF THE T-TEST OF MEANS*

Method of determination	Sample	Degrees of freedom	Calculated value of t	Critical value or range of t
Sulfate Sulfur, Long vs. Short	S-1	102	0.790	2.000 to 1.980
Extractions	S-2	100	4.475	2.000 to 1.980
Pyritic Sulfur, Short Extraction, Gravimetric vs. Titrimetric Determinations	S-1	70	0.106	2.000 to 1.980
	S-2	70	1.505	2.000 to 1.980
Pyritic Sulfur, Long Extraction, Gravimetric vs. Titrimetric Determinations	S-1	76	3.371	2.000 to 1.980
	S-2	72	0.007	2.000 to 1.980
Pyritic Sulfur, Short vs. Long Extractions, Gravimetric Determination	S-1	86	0.126	2.000 to 1.980
	S-2	83	0.953	2.000 to 1.980
Pyritic Sulfur, Short vs. Long Extractions, Titrimetric Determination	S-1	60	3.768	2.000
	S-2	59	0.552	2.008 to 2.000

*After a thesis by E. Fasig, Jr., Engineering Experiment Station, Ohio State University, Columbus, OH.

TABLE III. RESULTS OF THE F-TEST OF VARIANCES*

Method of determination	Sample	Degrees of Freedom		Calculated value of F	Critical range, F
		numerator	denominator		
Sulfate Sulfur, Long vs. Short Extractions	S-1	1	102	1.73	4.00 to 3.92
	S-2	1	100	26.97	4.00 to 3.92
Pyritic Sulfur, Long and Short Extractions	S-1	3	146	6.87	2.68 to 2.60
	S-2	3	142	2.96	2.68 to 2.60
Gravimetric and Titrimetric Determinations					

*After a thesis by E. Fasig, Jr., Engineering Experiment Station, Ohio State University, Columbus, OH.

Pyritic Sulfur (ASTM D-2492). Data determined by four methods (Table 1), were, for all cases except one, in close agreement with each other and were characterized by values of standard deviation, repeatability, and reproducibility, all of which were very similar. The precision of the titrimetric technique was better than that of the gravimetric procedure as shown by the values of standard deviation and reproducibility shown in Table I. Since the precision and results of the various methods are so similar, the advantages of the short, 30-minute extraction procedure over the long, 40-hour technique, and the greater ease and speed of the titrimetric determination in comparison with the gravimetric procedure make the method Pyritic Sulfur, Short Extraction, Titrimetric Determination the most suitable for use in the routine analysis of coal.

TOTAL SULFUR

The need for accurate methods of determining total sulfur in coal was previously noted. The Eschka and bomb washing procedures are the two most commonly used methods in the United States, both of which are given in ASTM D-3177 (6).

The Eschka procedure consists of thoroughly mixing coal with Eschka mixture (2 parts calcined MgO and 1 part anhydrous Na_2CO_3) and ashing it in a muffle furnace at 800°C . The ashed coal is leached with hot water, filtered, and the sulfur is determined gravimetrically in the filtrate. This method is rapid when carried out on large batches of samples; it is most accurate when used for coals containing no more than 6 or 7% sulfur.

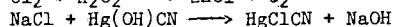
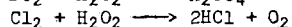
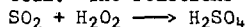
The bomb washing procedure is convenient for laboratories that make frequent coal calorimetric determinations as described in ASTM D-2015 (6). After cooling and careful venting, the bomb used for a calorific determination is thoroughly washed with water, and the sulfur is then gravimetrically determined in the bomb washings. This method gives excellent results when used for the analysis of coals containing no more than 4% sulfur.

A third method in common use, but which was dropped as an ASTM standard in 1974, is the peroxide bomb method (13). In this method, coal is fused with Na_2O_2 in a special bomb. Following dissolution of the melt, sulfur is usually determined gravimetrically. This procedure is especially useful for the determination of high sulfur concentrations up to 30 or 40%. The difficulties and precautions required for the correct use of these three methods have been described by Selvig and Fieldner (14) and Rees (15).

There are at least three other less frequently used procedures: The high-temperature combustion method (16), which has been approved by ASTM Committee D-5 and will probably be published in 1975; the Leco or induction furnace method, which was tested by ASTM Committee D-5 with unsatisfactory results (17); and X-ray fluorescence methods.

The high-temperature combustion procedure is most useful for the rapid (30 min. per sample) determination of total sulfur in a small batch of less than 8 or 10 samples. Under these conditions, it is much more rapid than the Eschka method; however, when samples are analyzed in larger groups (20 to 30 samples), the Eschka procedure is preferred over the high-temperature combustion method.

The high-temperature combustion method for determining total sulfur in coal is based on the procedure of Mott and Wilkinson (18) in which a weighed coal sample is burned in a tube furnace in a stream of oxygen at a temperature of 1350° C. The sulfur oxides and chlorine formed are absorbed in H₂O₂ solution yielding HCl and H₂SO₄. The total acid content is determined by titration with NaOH, and the amount of NaCl resulting from the titration of the HCl is converted to NaOH with a solution of mercuric oxycyanide (Hg(OH)CN). This NaOH is determined titrimetrically and used to correct the sulfur value, which is equivalent to the amount of H₂SO₄ formed during combustion of the coal. The reactions taking place are as follows:



The method is accurate for both low and high sulfur concentrations.

Finally, X-ray fluorescence has been used for determining total sulfur in coal (19,20,21). Ruch et al. (1) have recently described a method of preparing pressed coal samples, which may be used for the determination of a variety of major, minor, and trace elements, including sulfur, in whole coal. Their sulfur values for more than 100 coals showed good agreement with those determined by the ASTM standard Eschka procedure (Ruch, p. 15). The economy and speed of such X-ray fluorescence methods, when used for multiple determinations (e.g. Al, Si, Ca, Mg, Fe, K, Ti, P, and S) in the same prepared coal sample, are probably unsurpassed by any other method. The relative standard deviation for sulfur, as determined by the X-ray fluorescence method of Ruch et al. (1) is 0.5%.

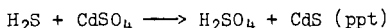
INSTRUMENTAL METHODS FOR DETERMINING PYRITIC SULFUR

The HNO₃ extraction of pyrite (FeS₂) from coal yields a solution ideal for the atomic absorption determination of iron as a measure of pyritic sulfur. Current studies of this method by ASTM Committee D-5, the U. S. Bureau of Mines, Pittsburgh, PA, and the TVA Central Chemical Laboratories, Chattanooga, TN, show good agreement between pyritic iron values determined using an atomic absorption procedure with those determined by the titrimetric methods described for pyritic iron in ASTM D-2492 (6). The method is simple and rapid, and it may soon replace currently specified ASTM standards. Care must be taken to avoid interferences from variable amounts of H₂SO₄ formed when pyrite is oxidized during extraction of the coal with HNO₃. Compensation for this matrix change can be made by adjustment of the sample size and addition of H₂SO₄ to standards, by addition of a flame buffer such as LaCl₃ to samples and standards, or both.

The determination of crystalline pyrite in coal by an X-ray diffraction method has been described by Schehl and Friedel (22). Finely ground coal samples of known pyrite concentration were used as standards in a technique that takes advantage of digital computers for measurement of the diffraction patterns, as well as for the calculation of the percentage of pyrite present in the coal sample. Background corrections due to carbon are made and quantitative results achieved by comparing the integrated intensity of a given pyrite reflection with the integrated intensity of a particular reflection from an internal standard (nickel). Acceptable precision within current ASTM tolerances was obtained for the coals studied, but interferences from reflections due to high concentrations of kaolin in coal were noted.

CHEMICAL REDUCTION METHOD FOR DETERMINING PYRITIC SULFUR

Methods involving reduction of pyrite to H_2S have also been employed for the determination of forms of sulfur (23,24,25). A reduction method (24) was recently studied by Kuhn et al. (26). This method uses lithium aluminum hydride to reduce pyritic sulfur to H_2S , which is then reacted with $CdSO_4$. The H_2SO_4 formed from the reaction



is titrated with standard base. Both sulfate and organic sulfur were determined by ASTM D-2492 procedures (6).

Major advantages of this method are that pyritic sulfur can be directly determined without danger of oxidation of the sulfur containing organic constituents, and that it can be determined without prior removal of sulfate sulfur. Further, it is extremely useful as an independent check on the accuracy of values for the forms of sulfur determined by the ASTM oxidation method.

ACCURACY OF FORMS OF SULFUR METHODS

Questions concerning the accuracy of either oxidation or reduction methods for the determination of forms of sulfur in coal generally stem from the difficulties associated with the incomplete extraction of finely-dispersed pyrite (25,27,28,29). Results of these studies have been at variance. In some cases, fine grinding of coal (-200 mesh) tended to increase the amount of pyrite extracted by HNO_3 , especially in high rank British coals (>85% carbon content). However, for U. S. coals, grinding to the usual -60 mesh particle size has been successful (7,8,9,10). Burns (30) also found fine grinding to be unnecessary for Australian coals when pyritic sulfur was extracted from the coal residue following the sulfate sulfur extraction rather than from a fresh coal sample.

These and other questions regarding the reliability of determinations of forms of sulfur were the subject of a recent investigation (26). For this study, results from the ASTM oxidative method were compared with those of a reductive method (24) to determine whether or not extraction of pyrite is complete, whether or not organic matter is significantly affected by HNO_3 extraction, and whether or not organic sulfur can be obtained either by computation or by Eschka determination of residual sulfur following HNO_3 extraction of pyritic sulfur. The influence of coal particle sizes (-60, -200, and -400 mesh) on the values determined by both methods was also studied.

Results for two coals, which are representative of the nine coals studied in this investigation, are given in Table IV. The principal conclusions are summarized as follows:

- 1) Coal particle size had no significant effect on total sulfur determined by the Eschka method (Table IV, column four).
- 2) X-ray fluorescence values for total sulfur agree well with Eschka values (Table IV, columns four and five).
- 3) Pyritic sulfur values determined by the ASTM method are not significantly influenced by coal particle size (Table IV, column seven).
- 4) For the reduction method, pyritic sulfur values in agreement with those from the ASTM procedure were obtained only when the coal was ground to -400 mesh (Table IV, columns seven and eight).
- 5) Agreement of total iron in the coals, as determined by X-ray fluorescence, with the sum of the iron determined in the ASTM HCl and HNO_3 extracts was excellent (Table IV, columns two and three). This indicates that all of the pyritic iron (sulfur) was extracted by the HNO_3 .
- 6) It was concluded that no pyritic iron remained in the residues of the nine coals studied after they were subjected to either the ASTM oxidation method or the reduction method (on -400 mesh coals only). Therefore, organic sulfur values calculated by subtracting the sum of sulfate sulfur plus pyritic sulfur from total sulfur were deemed accurate (Table IV, columns nine and ten).

TABLE IV. CONCENTRATION OF IRON AND VARIETIES OF SULFUR IN TWO ILLINOIS COALS

Sample and size	Total iron		Total Sulfur		Sulfur						
	(%)		(%)		(%)						
	X-ray fluorescence		X-ray fluorescence		SO ₄	Pyritic		Calculated organic		Determined organic	
	ASTM	ASTM	ASTM	ASTM		ASTM	Reduc.	ASTM	LAH	ASTM	Reduc.
C-18067											
-60	4.28	3.80	7.48	7.25	0.02	4.82	4.08	2.64	3.38	2.50	2.24
-200	4.26	4.28	7.53	7.45	0.02	4.76	4.44	2.75	3.07	2.48	2.21
-400	4.30	4.52	7.52	7.63	0.02	4.79	4.60	2.71	2.90	2.54	2.51
C-17167											
-60	1.24	1.23	2.91	3.05	0.40	0.94	0.77	1.57	1.74	1.37	1.45
-200	1.29	1.31	2.95	3.09	0.39	0.92	0.88	1.75	1.68	1.26	1.25
-400	1.30	1.31	2.93	3.07	0.39	0.93	0.93	1.61	1.61	1.19	1.31

ORGANIC SULFUR

Research on the nature and removal of organic sulfur compounds from coal has been extensive (31,32,33,34,35,36). Unfortunately, none of these investigations has led to useful methods for determining varieties of organic sulfur in coal. Indeed, as previously mentioned, no methods have as yet been developed for the direct determination of total organic sulfur in the presence of inorganic sulfates and sulfides. When organic sulfur has been "determined" rather than calculated by difference, the coal was first demineralized using methods similar to those described in the International Standards Organization Recommended Method R-602 (37), or by Kuhn et al. (26) and Smith and Batts (38). In these, sulfate and pyritic sulfur are first removed by acid dissolution, oxidation and/or reduction reactions. The total sulfur determined in the coal residue is then considered to be organic sulfur. This method was found to be fairly reliable by Kuhn et al. (26), although small losses of organic sulfur were unavoidable (Table IV, columns nine through twelve). The most accurate results for organic sulfur seemed to be those which were calculated.

An interesting new approach to the purported determination of organic sulfur in coal is that of Hurley and White (39). They employed a X-ray fluorescence method to first determine total sulfur from the K β line intensity and then a line ratio technique to find the proportion of sulfate sulfur (K β' line intensity) in the total sulfur:

$$\%S_{SO_4} = \% \text{ Total S} \times (SK\beta' / SK\beta) \times M_1$$

where M_1 is the slope of a standard straight line calibration curve of the ratio $(SK\beta' / SK\beta)$ vs. concentration. The peak shift of sulfur K β was used to determine amounts of sulfide and organic sulfur:

$$\%S_{org} = \% \text{ Total S} \times \left(\frac{\Delta SK\beta - B}{M_2} \right)$$

$$\%S_{pyr} = \% \text{ Total S} \times \left(100 - \frac{\Delta SK\beta - B}{M_2} \right)$$

where the calibration constants, M_2 and B are obtained from a straight line calibration curve of the form $Y = MX + B$. It should be noted that pyritic sulfur is a calculated difference figure, i.e., the sum of the three forms of sulfur must equal 100%. Therefore, the sulfur values are not independently determined.

NONPYRITIC SULFIDES

Studies have shown that some coals contain significant quantities of nonpyritic sulfide (1,2), and that it usually occurs in conjunction with high zinc concentrations (up to 5000 ppm). In the reduction method the pyrite (FeS_2) is first reduced to sulfide (FeS). Any nonpyritic sulfide present in the coal will contribute to the pyritic sulfur value when the chemical reduction of pyrite is carried out prior to

sulfate removal*. This is true only when the reduction step is done first, as some nonpyritic sulfide is lost in the HCl digestion for sulfate sulfur (ASTM). The ASTM method for pyritic sulfur measures only the pyritic iron. Consequently, a pyritic sulfur value determined by the reduction method that is higher than one determined by the ASTM method would be a measure of the amount of nonpyritic sulfide present in the coal. In such a case, Zn concentration is also a useful measure of nonpyritic sulfide.

The loss of nonpyritic sulfides as hydrogen sulfide in the hydrochloric acid digestion of sulfate sulfur (ASTM) would result in this sulfide's being determined as neither sulfate nor pyritic sulfur. The organic sulfur value, calculated as the difference between the total sulfur and the sulfate + pyritic sulfur values, would then be erroneously high.

ANALYSIS OF COAL-RELATED MATERIALS

Coal preparation and float-sink studies frequently require the determination of forms of sulfur in coal gravity fractions. Because these commonly contain 10 to 20% sulfur, care must be taken when applying methods developed for the analysis of whole coal to them. Helfinstine et al. (3,4) determined forms of sulfur in 64 Illinois coals, in their float fractions (five for each coal), and in the material that sank at a specific gravity of 1.60. These data were then used to calculate sulfur in the "raw coal" by proportionally combining the individual float-sink fractions to give values that should be equivalent to values given in the original raw coal analysis. The average difference in percent between analyzed raw coal sulfur values and those calculated from the individual analyses of float-sink fractions are -0.15, -0.05, and -0.11 for total sulfur, pyritic sulfur, and organic sulfur respectively. Although the means (as well as their standard deviations) are small and indicate good agreement, examination of all of the data shows notable exceptions for some high sulfur samples. In one coal, percent differences between analyzed and calculated values for total sulfur, pyritic sulfur, and organic sulfur were -0.56, -0.49, and -0.10, respectively. Careful resampling and analysis has shown that differences of this magnitude are not due to poor sampling or analytical techniques, but rather to small errors in the analysis of high sulfur materials using the ASTM method of determining forms of sulfur. Such errors may be magnified by factors of 10 or 20 in making the calculations.

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* For the reduction method, it was shown by Kuhn et al. (26) that pyritic sulfur can be determined in the presence of sulfate sulfur.

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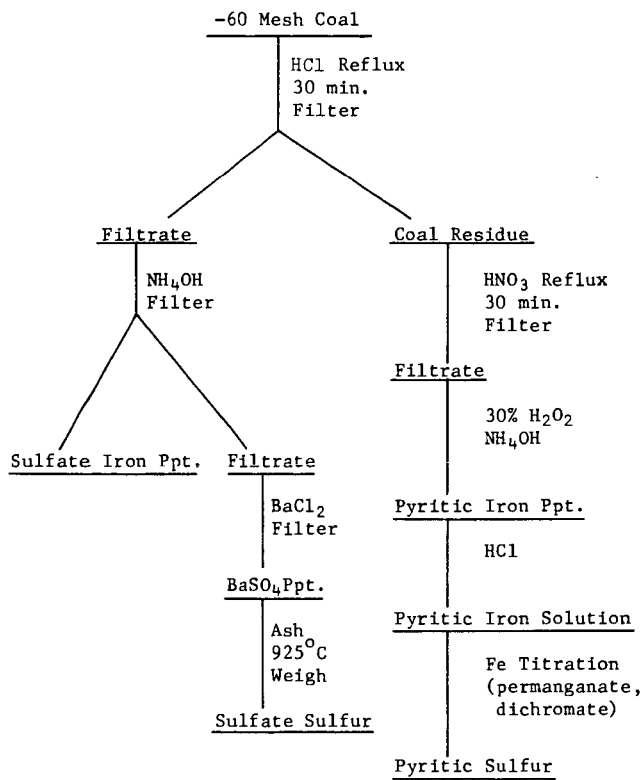


Figure 1. Flow diagram for ASTM determination of forms of sulfur in coal.

FATE OF ATMOSPHERIC SULFUR AND NITROGEN FROM FOSSIL FUELS

CHARLES HAKKARINEN*

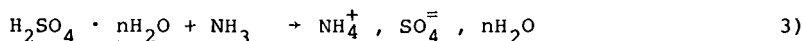
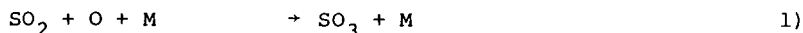
ELECTRIC POWER RESEARCH INSTITUTE, PALO ALTO, CALIFORNIA

Sulfur and nitrogen are emitted to the atmosphere during the combustion of coal and other fossil fuels principally as the gases sulfur dioxide (SO_2) and nitric oxide (NO). In uncontrolled systems, approximately 90% of the sulfur in the fuel is converted to SO_2 and 5% to SO_3 . The balance is emitted in flyash or collected in the bottom slag. (1) Coal combustion accounts for about 60% of the man-made sulfur oxide emissions (2,3), which represent 1/3 of the total global sulfur emissions to the atmosphere, viz. 300×10^6 tons SO_2/yr . (3) Nitrogen oxide emissions during fossil fuel combustion result from high temperature reaction of atmospheric nitrogen and oxygen, as well as partial combustion of nitrogenous compounds in the fuel. Important factors that affect NO production include: Flame and furnace temperature, residence time of combustion gases, rate of cooling, and presence of excess air. (1) Coal combustion accounts for 20% of the man-made NO emissions, which represent 1/10 of the 500×10^6 tons/yr produced by natural sources. (4)

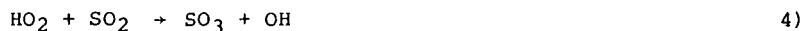
The atmospheric transport, conversion, and fate of sulfur dioxide and nitric oxide is quite complex. While qualitative descriptions of some conversion and deposition mechanisms are available, quantitative estimates of the importance of each mechanism remain crude.

Sulfur dioxide emitted into the atmosphere is advected and dispersed by the general air flow and smaller scale turbulence. Direct adsorption may occur on vegetation and soil surfaces (5). SO_2 may also be "washed out" in precipitation (6). However, it is generally believed that most SO_2 is chemically converted to sulfuric acid or a particulate, sulfate before removal from the atmosphere.

In the presence of sunlight, SO_2 may be oxidized in a three body reaction by photochemically produced monatomic oxygen. (7) Rapid hydration would follow to form a sulfuric acid mist. The presence of ammonia may buffer the reaction and increase production of sulfates. (8)



Other investigators (9, 10, 11) have recently proposed SO_2 reaction with either OH or HO_2 as an important homogeneous gas-phase conversion mechanism.



This mechanism has been purportedly demonstrated in laboratory experiments (11), but remains to be verified under actual field conditions. The development of a remote monitoring instrument for OH (9) should provide more information on its relative significance.

Direct photo-oxidation of SO_2 is considered to be negligible. (12)

Heterogenous reactions on solid or liquid surfaces represent a second important class of SO_2 oxidation mechanism. The presence of heavy metal ions, such as iron or manganese have been observed to catalyze the conversion of SO_2 to acid sulfates. (13) Oxidation rates are highly dependent on temperature and relative humidity.

Catalytic oxidation may also occur on dry surfaces. Novakor, et al. (14) have demonstrated catalytic formation of sulfate on carbon soot in the laboratory and have identified several sulfur compounds on the surface of carbon particulates collected in urban atmospheres.

Sulfur compounds emitted during combustion and converted to sulfates are ultimately removed from the atmosphere by dry deposition and precipitation. Although the removal rates are not well quantified, the atmospheric residence time is estimated to range between one and seven days. (3) Long range transport of sulfates may therefore extend to hundreds of kilometers from the SO_2 source. (15, 16, 17,18)

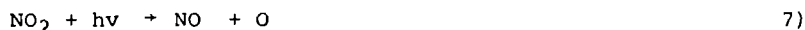
"Ballpark" estimates of net SO_2 to sulfate conversion rates for several mechanisms are listed below.

Table 1 SO_2 to SO_4 Conversion Rates

<u>Mechanism</u>	<u>SO_2 Consumption Rate</u>
Direct photo-oxidation	0.5 %/hr
Indirect photo-oxidation	1-3 %/hr
Air oxidation in liquid droplets	1-20 %/hr
Catalyzed oxidation in liquid droplets	1-20 %/hr
Catalyzed oxidation on dry surface	1-13 %/hr
Observed SO_2 consumption in a coal- fired power plant plume	
70% relative humidity	0.1 %/min
100% relative humidity	0.5 %/min

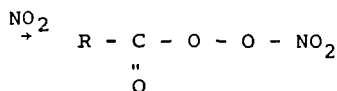
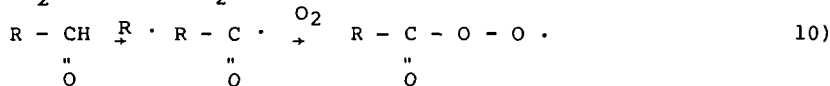
(Table adapted from 19, 20)

Nitrogen compounds are emitted during fossil fuel combustion principally as NO. Oxidation to NO₂ occurs very rapidly, however. Equilibrium values of NO and NO₂ are determined by the following reactions:



The NO/NO+NO₂ ratio is approximately .5 during daylight and .1 at night. (9)

NO may undergo a series of complex chain reactions (typically 100 times slower than the NO + NO₂ reaction) with olefinic hydrocarbons and hydroxyl radicals to form nitrate compounds. A typical sequence might be:



Measurements of nitrate ions in rain (21) suggest that NO₂ is transformed to nitrates in precipitation. However, the direct reaction



has not been shown to be significant in the atmosphere. (4) Two other mechanisms have been suggested recently (9) for nitrous and nitric acid formation during daylight:



Both mechanisms remain to be verified by field measurements of hydroxyls.

Heterogeneous surface catalysis of NO and NH₃ on carbon soot has been proposed by Chang and Novakov (22). In laboratory experiments they have generated volatile ammonium salts at ambient temperatures and reduced nitrogen compounds at elevated temperatures, in qualitative agreement with field observation at urban California sites.

Little information is available on the consumption rate of NO_2 by the mechanisms described. However, Robinson and Robbins have estimated the residence time of NO_2 to be three days, based on the total atmospheric nitrogen cycle. (23)

Acknowledgements

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REVIEW OF DESULFURIZATION AND DENITROGENATION IN COAL LIQUEFACTION

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INTRODUCTION

With ever increasing demands on fossil fuels as a source of energy and ever decreasing supplies of crude petroleum within the United States, the nation must turn more and more to the use of coal. Yet the people of this country have mandated through their representatives that they do not want the anticipated use of coal to degrade their environment.

The air pollutants of particular concern are nitrogen oxides, sulfur oxides and particulates. Nitrogen oxides are formed from nitrogen in air as well as organic nitrogen in the fuel, and their concentration is primarily a function of combustion parameters. Sulfur oxides and particulates are a function of the chemical composition of the fuel used.

In response to public demand, the Environmental Protection Agency, EPA, has established air quality standards which define maximum allowable concentrations of pollutants in the atmosphere. Individual states have established emission standards for existing sources which meet the EPA's Air Quality Standards while the EPA has established emission standards for new sources. The current Federal Standards for emissions for new fossil fuel fired steam generators larger than 250 million BTU/hr are presented in Table I.

Because nitrogen oxides are so dependent upon furnace operating parameters such as burner configuration, excess air used, air and fuel distribution, etc., it is difficult to predict the level of nitrogen oxides to be expected from a given fuel. On the other hand, reasonable predictions can be made of the expected SO_2 emissions from coal since the only source of SO_2 is the sulfur in the coal. Thus, we would expect that in order to meet the SO_2 emission standard for solid fuels of 1.2 lbs per million BTU's while burning 10,000 BTU/lb coal, the coal must contain 0.6 wt.% sulfur or less. Unfortunately, the sulfur content of coals ranges from 0.2 to over 10 wt.% while the typical coal contains 0.5 to 4 wt.% sulfur.

Sulfur in coal exists in three distinct forms; (a) as organic sulfur, (b) as pyrite or marcasite (two common crystal forms of FeS_2), and (c) as sulfates. The amount of organic sulfur is normally not over 3 wt.%. The sulfates, mainly calcium and iron, rarely exceed a few hundredths percent except in highly weathered or oxidized samples. Because pyrite and marcasite are difficult to distinguish, these forms of sulfur in the coal are called pyrite. Nitrogen in coal exists in organic form, and is generally in the range of 1.0 to 1.5 wt.%. A hypothesized structure which shows possible forms of organic sulfur and organic nitrogen in coal is shown in Figure 1.

COAL LIQUEFACTION

Process Description

One method that is being seriously considered to reduce sulfur and nitrogen contents of coal to acceptable limits is liquefaction in the presence of hydrogen. A conceptual flow diagram of such a process is shown in Figure 2. Coal mixed with a solvent and hydrogen reacts at elevated temperatures and pressure either in the absence or presence of a catalyst to form a mixture of liquid products. If hydrogen consumption is maintained at low levels, 1.5 - 3 wt.% of the coal fed, most of the product is a high boiling, heavy liquid with a heating value in the order of 16,000 BTU/lb. This

product is solid at room temperature and may be used directly as fuel if its sulfur content is less than 0.96 wt.% or further processed to form either gasoline or chemicals. Higher hydrogen consumption in the liquefaction reactor produces lower boiling products with lower levels of sulfur and nitrogen.

Organic sulfur and nitrogen are removed when coal is liquefied mainly by reactions which form H_2S and NH_3 . The ammonia can be recovered by conventional purification methods.

Hydrogen sulfide is normally recovered, concentrated, and then converted to sulfur in the Claus process. The effluent gas from the Claus unit must be further processed in a Claus tail gas cleanup unit to reduce sulfur compounds to an environmentally acceptable level. Hydrogen sulfide produced by gasification of coal or of unliquefied coal to produce hydrogen would normally be processed in that same equipment. Organic nitrogen compounds are converted almost completely to molecular nitrogen in high temperature gasification processes such as the Koppers-Totzek or Texaco.

In the liquefaction process, pyritic sulfur is reduced to FeS_x , where x is about 1.0. FeS_x is then removed mechanically by filtration or by solvent precipitation along with heavy liquid-like product and unconverted coal.

Desulfurization Results

Published data on the desulfurization of coal as a function of hydrogen consumption from the catalytic H-Coal, Gulf CCL, and Synthoil processes are presented for Illinois, Kentucky, Kaiparowits, Pittsburgh, Big Horn, Wyodak, and Middle Kittanning coals in Figure 3 (1,2,3,4,5). Analyses of these coals are presented in Table II. Published data from non-catalytic (SRC) processes are also presented in Figure 3 for Kentucky, Kaiparowits, and Illinois coals(5,6).

In general, the data plotted in Figure 3 show that as the total amount of hydrogen consumed increases, the sulfur content of the fuel oil product decreases. A band has been used to indicate the trend of all the catalytic data since this data has been taken over widely different combinations of reactor temperatures and pressures, coal space velocities, catalyst types, catalyst ages and activity levels with resulting wide differences in fuel oil yields. Consequently, no alleged superiority for hydrogen selectivity for sulfur removal of one catalytic system over another can be inferred from this particular collection of data.

Interestingly, the data plotted in Figure 3 show that the amount of hydrogen required to reach a moderate sulfur level of about 0.9 wt.% in large scale non-catalytic reactors corresponds reasonably well with the amount of hydrogen required to reach that same level of sulfur in catalytic systems. However, there may be larger differences in hydrogen consumption requirements between large-scale non-catalytic and catalytic processes at fuel oil product sulfur levels below about 0.5 wt.%. It should also be pointed out that the reactor residence times in non-catalytic systems corresponding to a given hydrogen consumption are much higher than the reactor residence times in catalytic systems at the same hydrogen consumption levels.

As hydrogen consumption will have a large effect on the economics of coal liquefaction processes, it would be advantageous if the process consumed hydrogen only in the formation of H_2S and NH_3 . Material balance calculations show that a hydrogen consumption equivalent to only 0.16 wt.% of the coal is required to convert 2.5 wt.% sulfur in the coal completely to H_2S and a hydrogen consumption equivalent to only 0.11 wt.% of the coal is required to convert 0.5 wt.% nitrogen in coal completely to NH_3 . However, as shown in Figure 3, the amount of hydrogen required to desulfurize coal to products containing sulfur levels of 0.5 - 1.0 wt.% is equivalent to 1.5 to 6.0 wt.% of the coal. A relatively larger amount of hydrogen is required to produce low sulfur fuel oil products from low sulfur subbituminous coals than from bituminous coals because subbituminous coals contain a much larger concentration of oxygen, 15 - 20 wt.%,

than bituminous coals which contain 7 - 12 wt.% oxygen. However, most of the hydrogen consumption shown in Figure 3 goes to the production of gaseous and liquid hydrocarbons with a hydrogen content of about 6 to 12 wt.% from coal with a hydrogen content of about 5 wt.%. Methane, for example, contains 25 wt.% hydrogen.

Although most of the data obtained from both catalytic and non-catalytic coal liquefaction falls within the band shown in Figure 3, a separate line has been drawn through data obtained from a bench scale non-catalytic flow reactor. The observed difference in the results obtained from the bench scale reactor and other reactors is not entirely due to differences in the coal processed. For example, there is a significant difference in the results obtained on the fraction of organic sulfur removed during the processing of a mixture of Kentucky No. 9 and No. 14 coals in the Wilsonville, Alabama six ton per day SRC plant and in the bench scale reactor, as shown below.

DESULFURIZATION RESULTS

	<u>Wilsonville (7)</u>	<u>Bench Scale</u>
Coal Processed	Kentucky No. 9 & No. 14	Kentucky No. 9 & No. 14
T, °F	830	825
P, psig	2400	2500
Space Time, hrs.	0.7	0.7
Fraction of organic sulfur removed, x	0.62	0.82

In order to explain the large observed differences in the fraction of organic sulfur removed in the two different reactor systems, the effect of mixing in the reactor was evaluated. Flow considerations indicated that the Wilsonville reactor may have acted essentially as a backmix reactor while the bench scale reactor may have acted essentially as a perfect plug flow reactor. However, neither a first order nor a second order kinetic rate plot fit the bench scale data.

In similar work, Lessley (8) suggested that the first order cracking rate coefficient in a non-catalytic system is a function of conversion. Applying a simplified form of the Lessley equation to the desulfurization bench scale data, a first order rate coefficient was assumed to have the following dependence on the fraction of organic sulfur removed, x;

$$k = k_o e^{-ax}$$

where k_o is an initial rate coefficient
and a is a constant

Assuming a first order reaction mechanism, values of " k_o " and " a " were obtained which would fit the experimental bench scale data. These results were then used to predict that if the reaction in the bench scale reactor had been carried out in a perfectly backmixed reactor, the fraction of organic sulfur removed under the reaction conditions specified in the preceding table would have been 0.58 rather than 0.62 actually observed. The fact that the Wilsonville reactor only approaches perfect backmixing was confirmed by the existence of a small temperature gradient in the reactor. The results of this analysis, based on limited data, suggest that the flow pattern of the fluid in the reactor may be an important variable.

After pyrite removal, overall reductions of up to 90% of the total sulfur in the original coal are possible. The sulfur levels of the various product fractions generally increase with boiling range. This is shown in Figure 4 for non-catalytic operation and Figure 5 for catalytic operations. Most of the sulfur is contained in the non-distillable ash free residual fraction to which an arbitrary mid-boiling point of 1100 or 1200°F has been assigned depending on the source of the data. These high boiling fractions may contain up to 1.2 wt.% sulfur when obtained from high sulfur bituminous coals.

Slurry oils produced during the non-catalytic liquefaction of high sulfur bituminous coals and boiling in the range of 450° to 900°F normally contain 0.2 - 0.4 wt.% sulfur. The sulfur content in the slurry oil produced from low sulfur subbituminous coals is normally less than 0.05 wt.%. An interesting, but unexplained anomaly, is indicated for narrow product fractions with a mid-boiling point between 350° and 450°F. These materials have sulfur contents higher than both lighter products and higher boiling products.

Denitrogenation Results

The amount of hydrogen required to obtain fuel oil products with a specific nitrogen content is indicated in Figure 6. There is a differentiation indicated on this figure between catalytic and non-catalytic processing results with higher nitrogen removal obtained catalytically. However, more hydrogen is required to obtain these lower product nitrogen levels. Even in the case of catalytic systems, the nitrogen content of the fuel oil fraction is seldom less than one half the nitrogen content of the feed coal. If higher levels of denitrogenation are required, additional hydrogen processing of the primary products using nitrogen specific catalysts will be necessary.

Figures 7 and 8 show nitrogen content as a function of the average boiling points of product fractions. These results show that there is a steady increase in nitrogen content as average boiling point increases. Surprisingly little difference is evident between the nitrogen contents of particular product fractions from catalytic and non-catalytic systems. However, as the yield of low boiling liquids is much larger from catalytic systems than from non-catalytic systems, the total nitrogen in all products from the catalytic systems is lower than the total nitrogen in all products from the non-catalytic systems.

CONCLUSIONS

Coal liquefaction can provide a low sulfur, environmentally acceptable fuel from high sulfur, environmentally unacceptable coal. However, current coal liquefaction processes require substantial amounts of hydrogen.

There is little difference in the amount of hydrogen consumed to reach a moderate sulfur level of about 0.9 wt.% in the fuel oil products from catalytic processes and in the fuel oil products from large scale SRC processes. There are indications that the hydrogen consumption requirements for desulfurization are significantly affected by the extent of mixing within the reactor.

A significantly larger amount of nitrogen is removed from coal processed in catalytic systems than from coal processed in non-catalytic systems. At the same time, the hydrogen consumptions and yields of low boiling liquids from catalytic systems are substantially larger than the hydrogen consumptions and yields of low boiling liquids from non-catalytic systems.

Finally, analyses of liquefied coal products indicates that the highest nitrogen and sulfur levels are contained in the highest boiling product fractions.

TABLE INEW STATIONARY SOURCE EMISSION STANDARDS

For Fossil Fuel Fired Steam Generators larger than 250×10^6 Btu/Hr.

<u>Species</u>	<u>Standard</u>
Particulates	a) $0.1 \text{ lb}/10^6 \text{ Btu}$ max. 2 hr. ave. b) 20% opacity. 40% opacity not more than 2 min/hr. c) Excludes H_2O
SO_2	a) Liquid Fuel: $0.8 \text{ lb}/10^6 \text{ Btu}$ max. 2 hr. ave. b) Solid Fuel: $1.2 \text{ lb}/10^6 \text{ Btu}$ max. 2 hr. ave.
NO_x	a) Gas Fuel: $0.2 \text{ lb}/10^6 \text{ Btu}$ max. 2 hr. ave. b) Liquid: $0.3 \text{ lb}/10^6 \text{ Btu}$ max. 2 hr. ave. c) Solid: $0.7 \text{ lb}/10^6 \text{ Btu}$ max. 2 hr. ave.

TABLE 2

COAL PROPERTIES

	-----Bituminous-----						-----Subbituminous-----		
	Kentucky	Illinois	Pittsburgh	Middle			Kaiparowits	Big	Wyodak
	#4	#9,11, 12,13	#6	#8	#8	Kittanning		Horn	
<u>Proximate</u>									
<u>Analysis</u>									
<u>Wt. %</u>									
Ash	8.5	17.2	11.6	8.3	8.3	9.7	6.3	4.4	7.3
Volatile Mater	39.2	37.8	42.0	34.1	42.8	40.3	43.9	42.5	46.4
Fixed Carbon	52.3	45.0	46.4	57.6	48.9	50.0	49.8	53.1	46.3
<u>Ultimate</u>									
<u>Analysis</u>									
<u>Wt. %</u>									
Hydrogen	5.1	4.8	4.8	5.1	5.1	5.3	5.1	4.6	4.8
Carbon	73.0	60.7	70.2	76.8	73.9	72.8	72.5	69.4	66.0
Nitrogen	1.3	1.2	1.4	1.6	1.2	1.3	1.0	1.2	1.1
Oxygen	9.0	11.3	9.3	6.7	7.5	7.5	14.7	19.9	20.4
Sulfur	3.1	5.5	3.2	1.5	4.0	3.1	0.4	0.5	0.4
Ash	8.5	16.5	11.1	8.3	8.3	10.0	6.3	4.4	7.3
<u>Forms</u>									
<u>of</u>									
<u>Sulfur</u>									
<u>Wt. %</u>									
Sulfate	0.26	0.47		.66	0.00	0.01	0.02		.14
Pyritic	1.42	3.08			2.1	1.32	0.00		
Organic	1.35	1.95		.83	1.9	1.77	0.38		.40

Figure 1 A REPRESENTATION OF BITUMINOUS COAL STRUCTURE

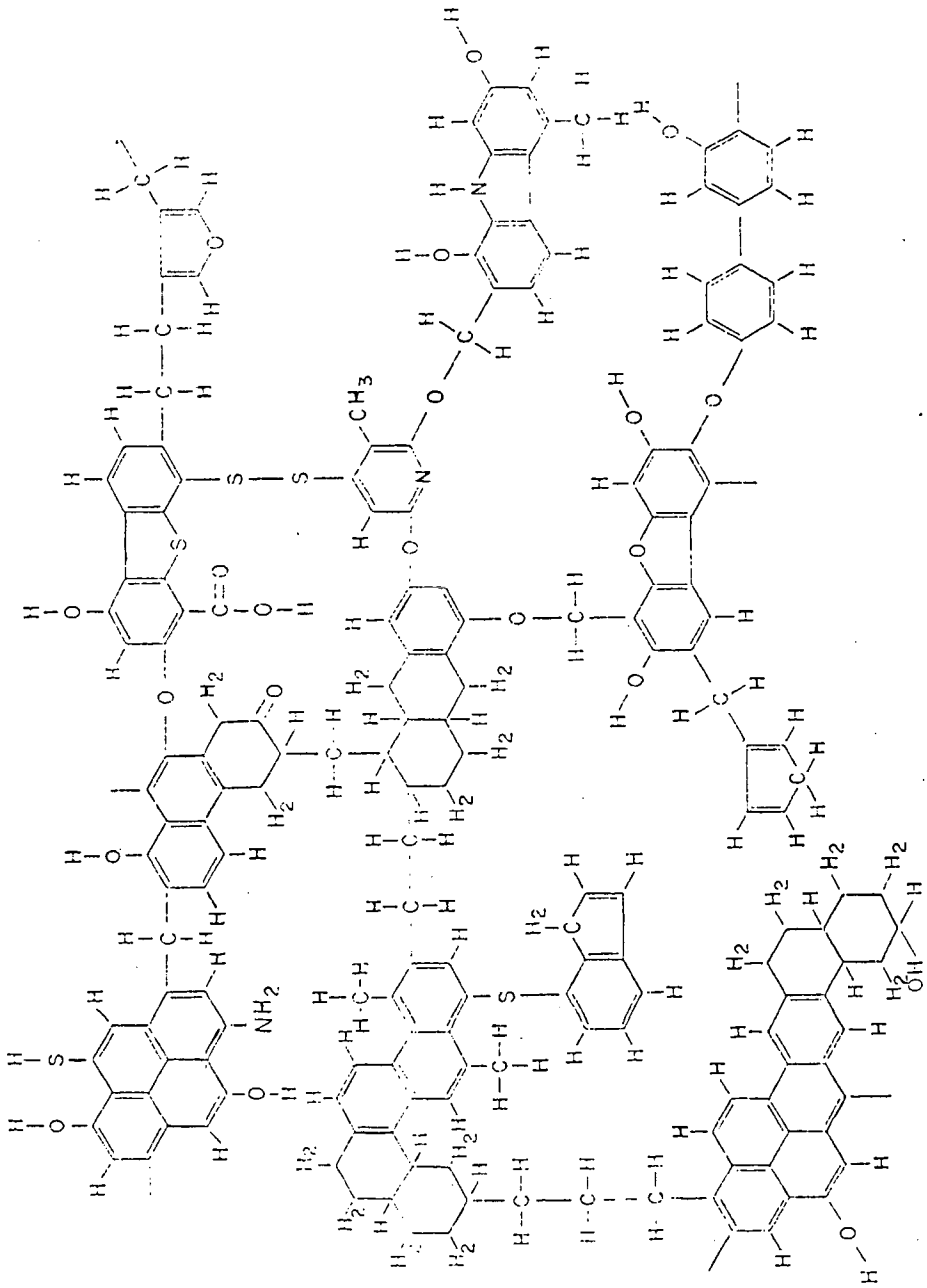


Figure 2 CONCEPTUAL COAL LIQUEFACTION PROCESS

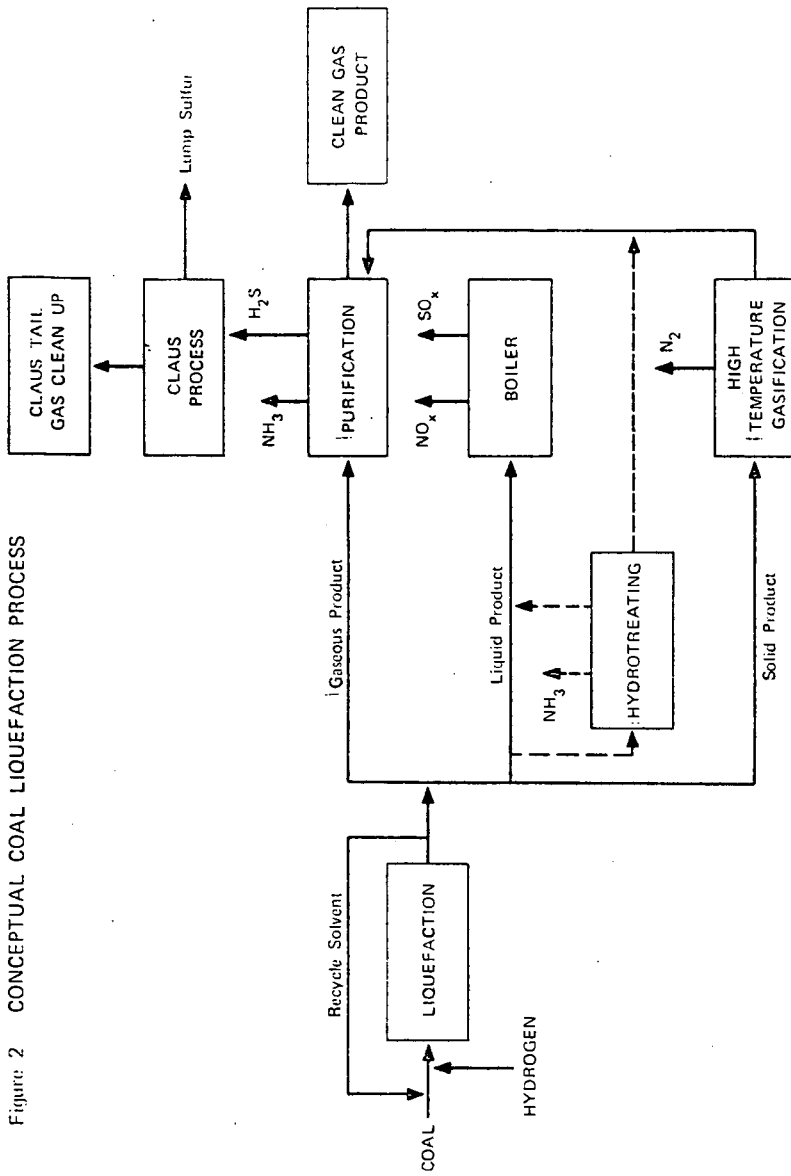


Figure 3 HYDROGEN REQUIRED TO PRODUCE LOW SULFUR FUEL OIL

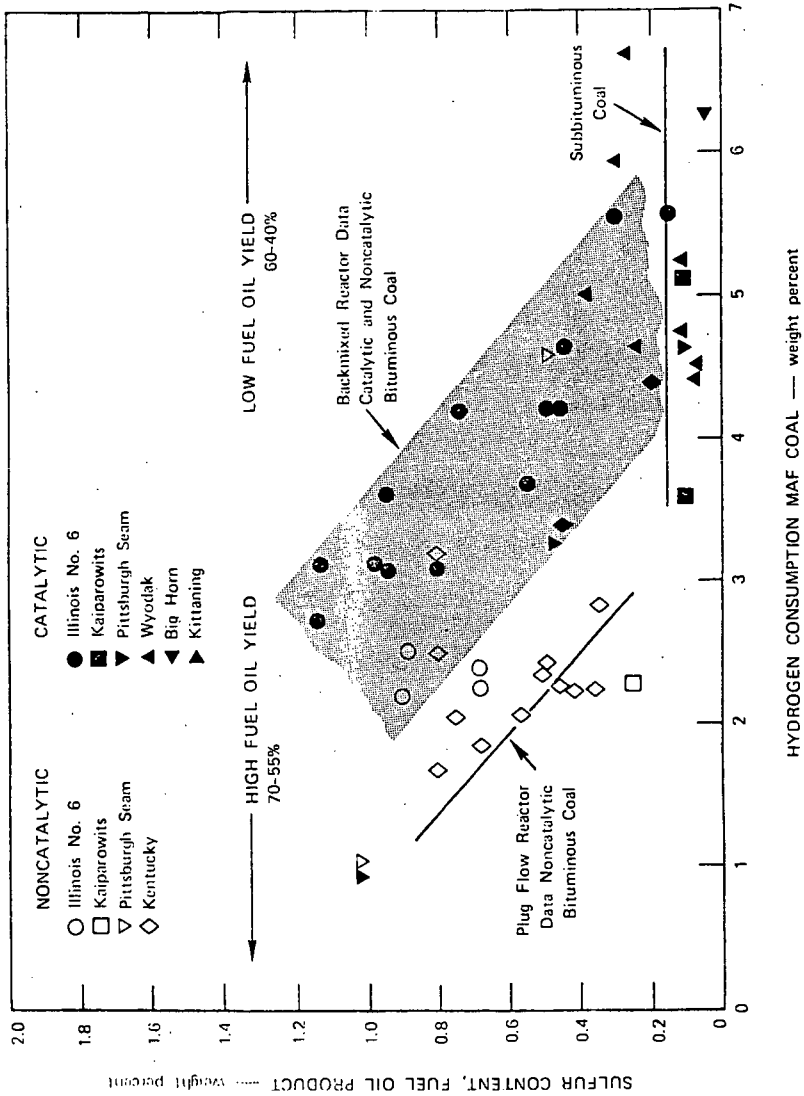


Figure 4 SULFUR CONTENT OF COAL LIQUIDS
FROM NONCATALYTIC OPERATIONS

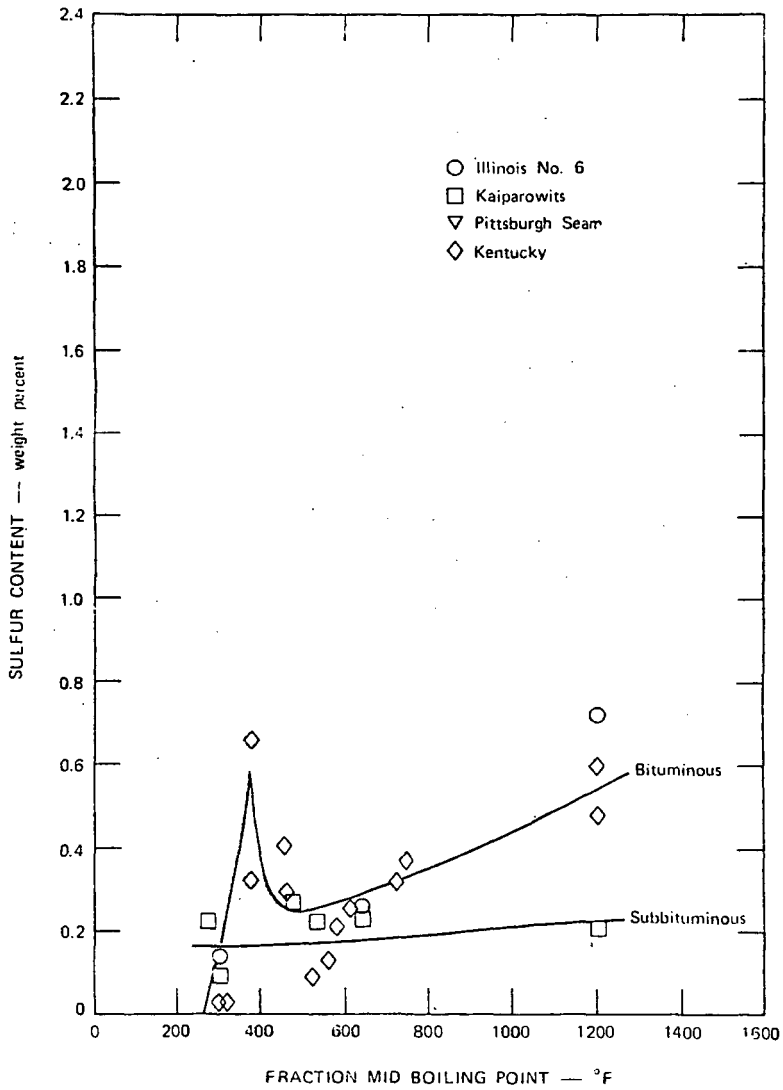


Figure 5 SULFUR CONTENT OF COAL LIQUIDS
FROM CATALYTIC OPERATIONS

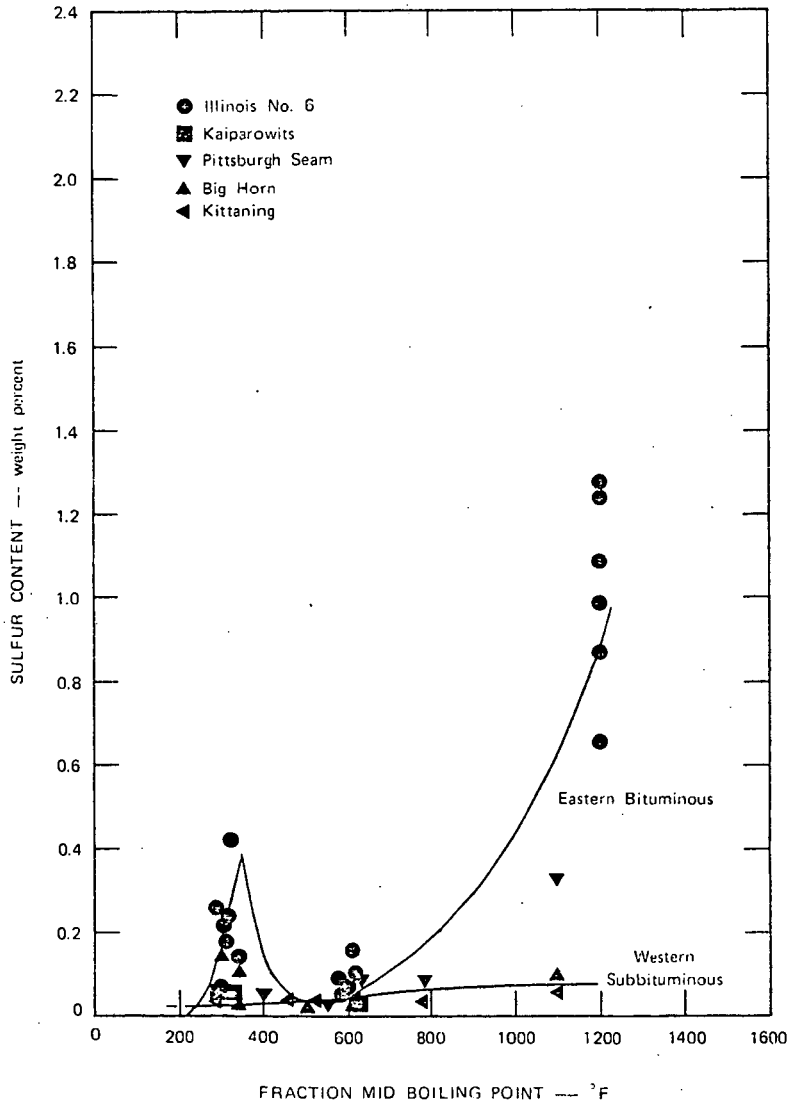


Figure 7 NITROGEN CONTENT OF COAL LIQUIDS
FROM NONCATALYTIC OPERATIONS

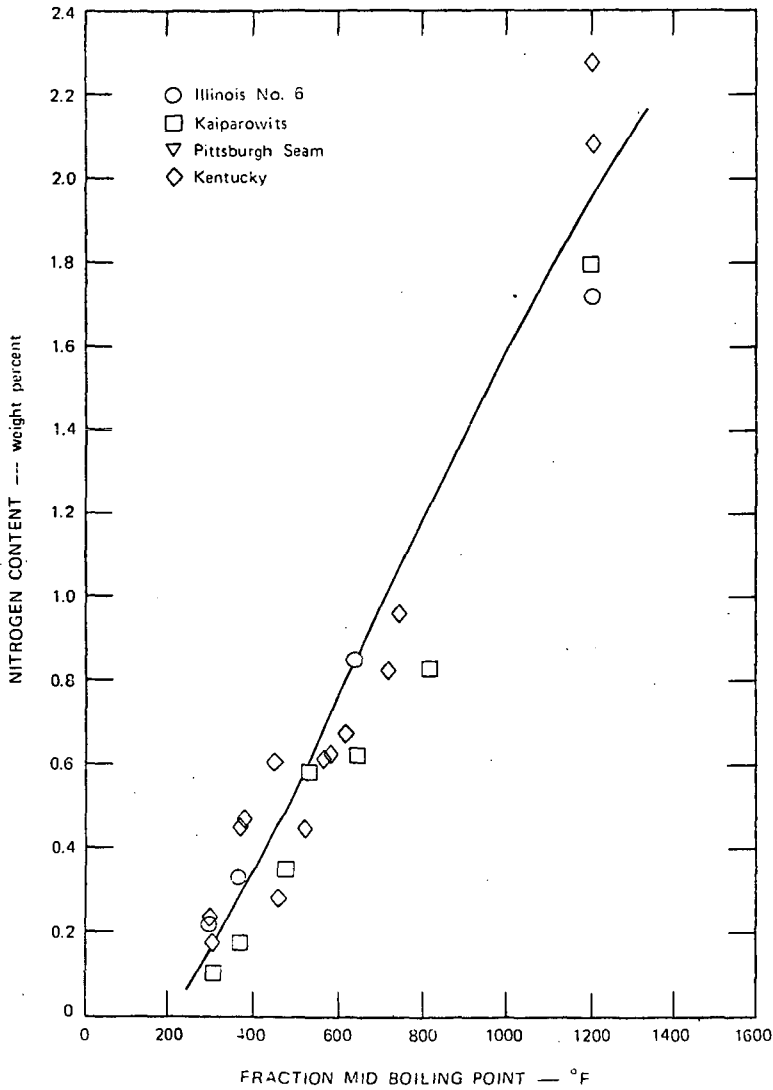
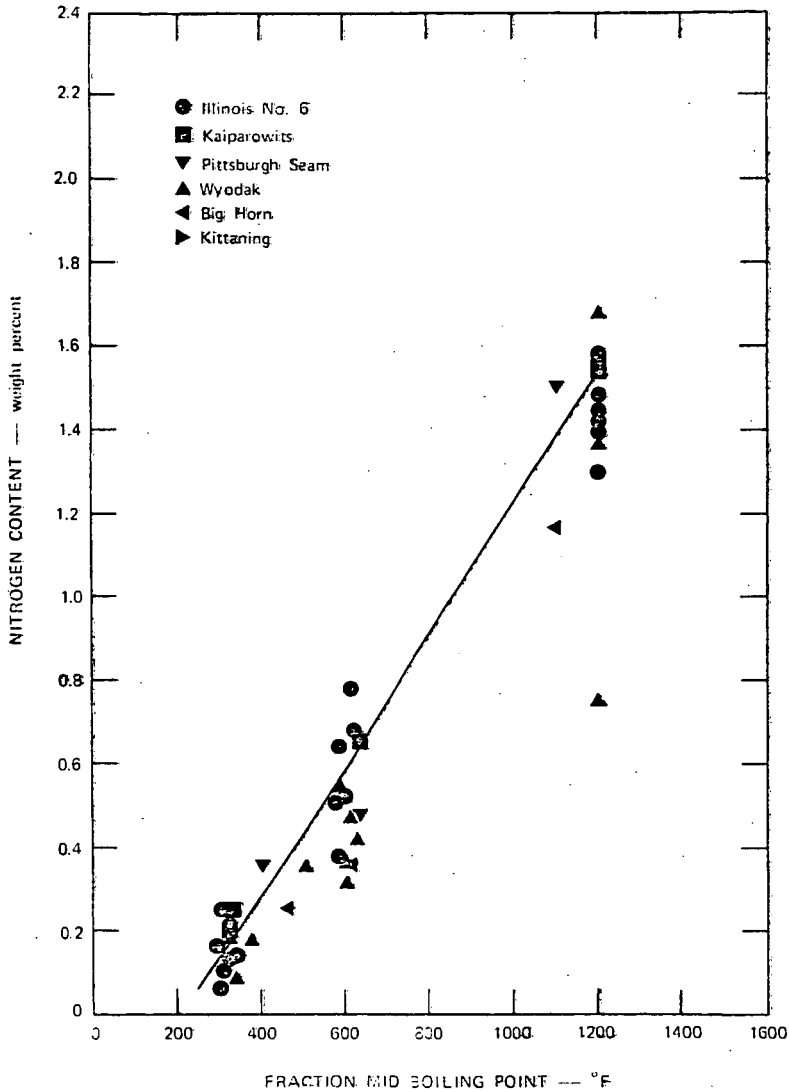


Figure 8 NITROGEN CONTENT OF COAL LIQUIDS FROM CATALYTIC OPERATIONS



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CHARACTERIZATION OF NITROGEN COMPOUNDS IN TAR PRODUCED FROM UNDERGROUND COAL GASIFICATION

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INTRODUCTION

In the fall of 1972, the Laramie Energy Research Center of the Bureau of Mines (now the Energy Research and Development Administration) initiated an in situ coal gasification experiment in Hanna, Wyoming. The objective was to ascertain if a low-Btu gas which would be competitive with other energy sources could be produced using present technology. If such a process were feasible it could provide an alternative to the hazards, costly transportation, and environmental objections of current coal mining technology.

The idea of underground coal gasification is over a hundred years old and has been tried in several different countries, with the largest experiments in the USSR, Great Britain and the U. S. These experiments showed that gasification was possible and a combustible fuel could be produced, yet the British and U. S. trials were determined to be economically impractical at the time they were conducted. Although information is sketchy, the USSR is presently generating electricity from low-Btu gas generated via in situ gasification. It is claimed that this power is generated at costs competitive with coal fired power plants.

DESCRIPTION OF THE UNDERGROUND GASIFICATION EXPERIMENT

The Hanna, Wyoming, experiment (1-3) was conducted in a subbituminous coal seam thirty feet thick at a depth of four hundred feet. A pattern of sixteen wells was drilled into the seam to take advantage of the natural fractures and permeability of the coal. In March 1973 the coal was ignited and air was supplied as the gasification agent. After initial start-up a steady-state system was obtained which lasted from September 1973 through February 1974. During this six-month period, gas analyses were taken along with other operating data. A low-Btu gas averaging approximately 130 Btu/scf was produced and the production was controlled to some degree by varying pressure and flow rates of the air injected and the gases produced.

In conjunction with low-Btu gas production, a liquid product was condensed from the gas stream. The major part was water but approximately 10% was an organic layer or coal tar. This coal tar has been estimated to contain 5% of the total energy produced from the in situ system. This coal tar raised three questions. What was its value as a petroleum substitute, either as a fuel or as a petrochemical feedstock? What information could be derived from this coal tar concerning reaction conditions occurring in the coal seam? Did the coal tar contain compounds which may lead to environmental damage? Characterization of these coal tars was therefore undertaken in an attempt to answer these questions.

During the period of gas production coal tar samples were collected from the produced gas stream. The liquid condensate, composed of coal tars and water, was separated in an air cooled condenser and a portion was drawn off as a sample. Two of these samples which represented distinctly different operating conditions during the life of the in situ coal gasification experiment were chosen for characterization.

The dry gas production rate over an eight-month period is shown in Figure 1 with the collection dates for samples 1 and 2 shown. As can be seen, Sample 1 was taken during a period of low gas production, which is associated with carbonization rather than gasification. Sample 2 was taken during a period of high gas production when the contribution of gasification was greater. A further indication of the relative contributions of carbonization and gasification can be seen from the gas analyses shown in Table 1 for the dates of coal tar sample collection. The carbonization of coal produces a large amount of methane compared to the amount of carbon monoxide. Upon reaching the conditions required for gasification, the carbon monoxide produced will increase due to the reactions shown by Equations 1 and 2.



TABLE 1. - Gas Analyses on Collection Dates

	Sample 1 August 4, 1973	Sample 2 December 10, 1973
Hydrogen	9.5 ^a	16.14
Argon	1.17	1.01
Nitrogen	55.62	53.84
Methane	9.62	3.74
Carbon Monoxide	0.80	6.94
Ethane	0.81	0.28
Carbon Dioxide	21.90	17.91
Propane	0.16	0.08
Propene	0.12	0
n-Butane	0.01	0
iso-Butane	0.05	0
Hydrogen Sulfide	0.23	0.05
Heating Value	154 Btu/scf	119 Btu/scf

^aValues are expressed in mole %

The high ratio of methane to carbon monoxide in the product gas on the collection date for Sample 1 indicates that carbonization is the primary reaction mode. Conversely, the low ratio of methane to carbon monoxide on the collection date for Sample 2 indicates that gasification was occurring to a greater degree.

Experimental

Nonaqueous titration of nitrogen was performed in acetic anhydride and benzene with HClO_4 as described by Buell (4). GLC analyses of tar bases were done on a 15' x .18" 15% TRITON X-305 on a Gaschrom P column. With a helium carrier gas, a flow rate of 46 ml/min STP, isothermally at 100°C for 16 min, then a 2°C/min

increase to 220°C, a useable separation of components resulted. NMR spectra were recorded on a Varian HA-100 instrument with the use of a Varian C1024 (CAT) console for one specific sample. UV spectra were recorded on a Beckman DB-G spectrometer with cyclohexane as solvent. Mass spectra were obtained on an AEI MS-12 instrument. Simulated distillations were performed with use of gas chromatography with residue defined as any material that does not boil below 1000°F. Fractionalization into tar acid, tar base and neutral fractions was accomplished by mineral acid and sodium hydroxide extraction and then regeneration through pH adjustment.

Coulometric nitrogen determination was performed on a Dohrmann instrument by reductive pyrolysis and subsequent ammonia titration in a microcoulometer. Coulometric sulfur determination was obtained using a Dohrmann instrument by oxidative pyrolysis to sulfur dioxide and titration of the sulfur dioxide in a microcoulometer.

COAL TAR CHARACTERIZATION

Each sample was subjected to analyses by simulated distillation, nonaqueous titration, and elemental analysis, plus determination of some physical properties. Upon separation of both samples into tar base, tar acid and neutral fractions, each fraction was then subjected to nonaqueous titration and coulometric determination of nitrogen and sulfur. The tar base fractions from both samples were separated by GLC where compound types have been assigned to separated components with specific structures identified in some cases.

Simulated Distillations

Simulated distillations showed Sample 1 to have a boiling range of 100-600°F with no residue. Sample 2 had a boiling range of 100-950°F with no residue. The percentage of the coal tar within a specified boiling range is shown in Table 2. As Table 2 shows, over 50% of sample 2 has a boiling distribution between 500°F and 700°F, while sample 1 has almost 50% of the boiling range distribution between 400°F and 500°F. This shows that sample 1 was a lighter coal tar than sample 2 and that the average molecular weight of sample 1 was less than sample 2.

TABLE 2. - Boiling Range Distribution

Sample	100 - 400°F	400 - 500°F	500 - 600°F	600 - 700°F	700 - 800°F	800 - 900°F	900 - 1000°F	Residue
1	30.0%	46.7%	22.0%	1.3%	0%	0%	0%	0%
2	6.2	16.9	25.6	28.2	16.0	5.3	1.8	0
Carbonized	0	11.3	16.3	13.1	15.2	12.4	7.5	24.2

For comparison, the boiling range distribution for the coal tar produced by laboratory carbonization of a Hanna coal sample at 500°C is presented. In comparing the distribution of material depicted in Table 2 the relative amount of residue becomes evident. Samples 1 and 2 show no residue while nearly a fourth of the carbonized sample is residue or material boiling above 1000°F. This demonstrates a unique fact concerning these coal tars. While the underground gasification may be similar to aboveground gasification, the coal tars produced in underground gasification are carried to the surface as a steam distillate. Since very little heavy tar will reach the surface, under these conditions, very little if any residue is expected, and the coal tar will not be entirely representative of the total tar generated in the combustion zone.

Nonaqueous Titrations

Nonaqueous titrations of samples 1 and 2 are shown in Table 3.

TABLE 3. - Nonaqueous Titrations of Samples 1 and 2

Sample 1	0.665% WB ^a	0.129% VWB ^a
Sample 2	0.524% WB	0.186% VWB

^aWB and VWB refer to weak and very weak base

Strong, weak, and very weak bases are defined by their half neutralization potentials (HNP), with strong bases having an HNP less than 150 mV, weak bases between 150 and 350 mV, and very weak base greater than 350 mV. Examples of weak bases would be pyridines or quinolines while amides would be titrated as very weak bases. Primary and secondary anilines titrate as very weak bases since they will acetylate and then titrate as amides. It should be understood that not all nitrogen compounds will titrate. Conversely not only nitrogen containing compounds will titrate, as an example, some sulfoxides titrate as very weak bases.

Physical Properties

Some of the physical properties of samples 1 and 2 are shown in Table 4. As expected from the conclusions of the simulated distillations, sample 2 is a heavier sample. The higher specific gravity, viscosity and heat of combustion all indicate that Sample 2 does indeed represent a higher average molecular weight coal tar.

TABLE 4. - Physical Properties

	Sample 1	Sample 2
Specific gravity at 60°F	0.962	0.977
Viscosity at 100°F	3.55 centistokes	13.16 centistokes
Heat of Combustion	16,073 Btu/lb	17,256 Btu/lb

Elemental Analyses

The elemental analyses of samples 1 and 2 indicate a marked difference in oxygen content as shown in Table 5.

TABLE 5. - Elemental Analyses

	Sample 1	Sample 2
Carbon	77.80	86.33
Hydrogen	10.22	10.43
Nitrogen	0.74	0.79
Sulfur	0.23	0.18
Oxygen	11.04 ^a	2.27 ^a

^aOxygen percentage is determined by difference

This change in oxygen content is attributed to the relative amounts of tar acids in each sample. This is shown in Table 6, where the composition of samples 1 and 2 vary noticeably with respect to the relative amounts of tar acids. Preliminary mass spectral analysis of the tar acid fraction from Sample 1 showed the majority of the fraction to be substituted phenols which would help explain the higher oxygen content in sample 1 compared to sample 2.

TABLE 6. - Composition of Coal Tar, by Weight Percent

	Sample 1 ^a	Sample 2 ^b
Tar Base	4.0	8.7
Tar Acid	42.1	14.5
Neutral	53.9	76.8

^a90.9% recovery of sample 1

^b96.4% recovery of sample 2

The difference in tar acid content between the two samples is proposed to be due to some basic change in the conditions producing the two samples. At the time Sample 1 was produced, the air injection rate into the combustion zone was considerably less than at the time Sample 2 was formed. Higher air injection rates are associated with higher coal utilization, higher gas production rate, and higher exit temperature of the produced gas. This would suggest that the coal tars collected in Sample 2 either were being formed at higher temperatures or were passing through a higher temperature flame front (combustion zone). Fieldner and Davis (5) have reported a change in composition of coal tar with increasing carbonization temperature. They stated that increasing temperature causes a decrease in tar acid content which agrees with the comparison of Samples 1 and 2 (Table 6). With the increase in boiling range and other parameters measured during the experiment, this evidence indicates that Sample 2 was indeed produced at a higher temperature than Sample 1.

Total Nitrogen, Total Sulfur and Nonaqueous Titration
of Base, Acid and Neutral Fractions

The results of coulometric determination of nitrogen and sulfur plus the nonaqueous titrations of the tar base, tar acid and neutral fractions of samples 1 and 2 are shown in Table 7.

TABLE 7. - Total Nitrogen, Total Sulfur, and Titratable Nitrogen for Acid, Base and Neutral Fractions

	Total Sulfur	Total Nitrogen	Titratable Nitrogen ^a
Sample 1			
Tar Base	0.00%	9.64%	8.10% WB, 1.36% VWB
Tar Acid	0.33	0.35	0.264% WB, 0.081% VWB
Neutral	0.02	0.08	0.035% VWB
Sample 2			
Tar Base	0.23	4.82	4.45% WB, 0.36% VWB
Tar Acid	0.14	0.09	0.058% VWB
Neutral	0.20	0.37	0.037% WB, 0.145% VWB

^aWB and VWB refer to weak and very weak base

As can be seen from Table 7, the distribution of sulfur in the separate fractions seems to be random and therefore no conclusions have been drawn as to their compound types or explain their distribution. An interesting point about the nitrogen values is the fact that while sample 2 contains approximately twice the weight percent tar base that sample 1 contains, the total nitrogen of sample 2's tar base fraction is about half that of sample 1's tar base fraction. This would suggest that the tar bases in sample 2 have a higher average molecular weight than those of sample 1.

The nonaqueous titrations of the two different tar base fractions indicate the possibility of pyridines and quinolines as weak bases with the added possibility of anilines titrated as very weak base.

Identification of Selected Components in the Tar Base Fraction

Twelve different components were fractionated by GLC from Sample 1 and spectral data were obtained on each. These twelve peaks constituted 69% of the base fraction of Sample 1. Compound types have been assigned to all separated components and specific structures in some cases. Assignments were accomplished with the combined aid of NMR, MS, UV and GLC data. The results are tabulated in Table 8.

TABLE 8. - Tabulated Spectra on Separated Components From
Tar Base Fraction of Sample 1

Component	t_R^a	% Total of Base Fraction	NMR Predominant Peaks	UV	MS	Compound Type or Compound
1	8.9	1.18%	Triplet- δ 7.10; Triplet- δ 7.50; Doublet- δ 8.45	λ_{max} at 262 nm	100% m/e 79	pyridine
2	11.0	6.40	Singlet- δ 2.41; Quartet- δ 6.95; Triplet- δ 7.36; Doublet- δ 8.33	λ_{max} at 257 nm	100% m/e 93	2-picoline
3	13.1	6.20	Singlet- δ 2.37; Doublet- δ 6.74; Triplet- δ 7.24	λ_{max} at 260 nm	100% m/e 107	2,6-lutidine
4	14.9	9.61	Triplet- δ 1.24; Singlet- δ 2.24; Quartet- δ 2.72; Multiplet- δ 6.98; Multiplet- δ 7.35; Singlet- δ 8.30	λ_{max} at 255 nm	90% m/e 93 10% m/e 107	3-picoline, 4-picoline and 2-ethyl pyridine
5	17.3	12.90	Triplet- δ 1.21; Singlet- δ 2.17; Singlet- δ 2.36; Quartet- δ 2.65; Multiplet- δ 6.77; Multiplet- δ 7.22; Doublet- δ 8.17	λ_{max} at 258 nm	90% m/e 107 8% m/e 121	2,4-lutidine, 2,5-lutidine plus some methyl ethyl pyridine
6	18.3	3.22	Singlet- δ 2.18; Singlet- δ 2.36; Multiplet- δ 6.81; Doublet- δ 7.19; Singlet- δ 8.15	λ_{max} at 263 nm	90% m/e 107	2,3-lutidine

TABLE 8. - Tabulated Spectra on Separated Components From Tar Base Fraction of Sample 1 (Continued)

Component	t _R ^a	% Total of Base Fraction	NMR Predominant Peaks	UV	MS	Compound Type or Compound
7	19.2	7.11	Triplet- δ 1.21; Singlet- δ 2.14; Singlet- δ 2.32; Quartet- δ 2.59; Singlet- δ 6.58; Doublet- δ 7.34	λ_{\max} at 262 nm	15% m/e 107 79% m/e 121	trimethyl pyridine and an ethyl pyridine
8	31.1	5.98	Broad Singlet- δ 3.36; Quartet- δ 6.52, Triplet- δ 6.96	λ_{\max} at 283 nm λ_{\max} at 231 nm	93% m/e 93	aniline
9	34.7	4.88	Singlet- δ 2.15; Broad Singlet- δ 3.28; Multiplet- δ 6.32; Triplet- δ 6.84	λ_{\max} at 285 nm λ_{\max} at 235 nm	97% m/e 107	2-methylaniline
10	38.1	2.54	Triplet- δ 1.15; Singlet- δ 2.10; Quartet- δ 2.45; Broad Singlet- δ 3.32; Multiplet- δ 6.25; Triplet- δ 6.86	λ_{\max} at 286 nm λ_{\max} at 235 nm	92% m/e 121	a dimethyl aniline and an ethylaniline
11	39.1	4.08	Doublet- δ 1.15; Singlet- δ 2.05; Multiplet- δ 6.10 to δ 8.10; Singlet- δ 8.80	λ_{\max} at 313 nm λ_{\max} at 270 nm	63% m/e 129; 16% m/e 121; 9% m/e 135; 8% m/e 94	quinoline, a dimethyl aniline and a trimethyl aniline
12	40.5	5.02	Triplet- δ 1.12; Quartet- δ 2.40; Singlet- δ 2.62; Doublet- δ 2.75; Multiplet- δ 7.04 to δ 8.00; Singlet- δ 8.78	λ_{\max} at 315 nm; λ_{\max} at 265 nm	45% m/e 143; 22% m/e 135; 17% m/e 129; 12% m/e 157	a methyl quinoline, a C ₃ aniline; quinoline, a dimethylquinoline

^aGLC retention times are relative to air

As can be seen from the data presented, all the components separated were not pure compounds, but a compound type can be determined from the spectrographic data. The resolution of the GLC tended to drop off as the heavier components were eluted. Due to the more complex nature of their spectra and the greater number of possible structures, specific structures have not been assigned to some of these heavier components.

46.6% of the base fraction was substituted pyridines, 13.4% anilines, and 9.1% quinolines. The majority of the remainder is probably substituted pyridines since

they are eluted after component #7 and before #8 which is aniline. Comparing this analysis with the work of Karr, et.al. (6), who found the majority of the tar base fraction of a low temperature coal tar to be quinolines, indicates that this coal tar was produced under conditions other than those producing low temperature coal tars.

The base fraction from Sample 2 was also subjected to identical GLC analysis as the base fraction from Sample 1. This sample also showed a wide distribution of components except that the majority of the fraction was much heavier than that from Sample 1. The GLC trace indicated six resolved peaks with retention times from 39.5 to 46.6 constituting approximately 45% of the base fraction. Comparing these retention times with those in Sample 1 suggests that these components are alkylated anilines or quinolines.

NMR spectra of five of these six peaks indicate these components to be substituted quinolines. As yet, no specific structures have been assigned to any of the peaks. This would agree with Karr's work and would suggest that the coal tars are formed under low temperature conditions. However, with other evidence already presented, such as boiling range, production rates, gas exit temperatures and tar acid content, it is believed that Sample 2 could not have been produced at lower temperatures than Sample 1.

CONCLUSIONS

In summary, the composition of the coal tar, particularly the basic fraction, is reasonably well known. A decision on its use as a petrochemical feedstock might be made from this information. However, the conditions under which the coal tar is produced are still unknown. Improved monitoring of the combustion zone, especially temperatures, will be included in future experimentation at Hanna. Data from this additional monitoring should allow more definite conclusions to be drawn. Possible herbicidal properties of components identified would require precautions against spillage to minimize environmental impacts. Monitoring underground migration of these organic fluids to determine what effect they may have on water supplies is being studied.

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NOTE: Any reference to specific brand names does not imply endorsement by the Bureau of Mines.

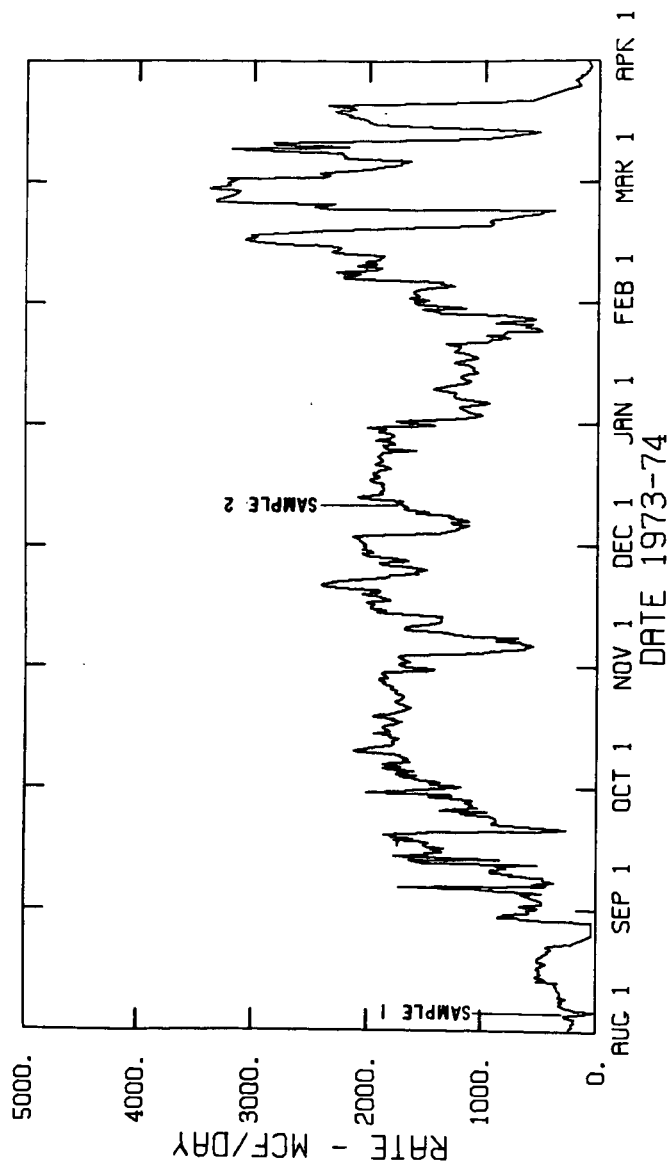


FIGURE 1. - DRY GAS PRODUCTION RATE, UNDERGROUND COAL GASIFICATION
EXPERIMENT, HANNA, WYOMING

LOWERING THE SULFUR AND ASH CONTENTS OF HIGH-SULFUR COALS BY PEROXIDE-ACID TREATMENT

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INTRODUCTION

Considerable effort has been devoted in recent years to upgrading high-sulfur coals by both physical and chemical methods. Some methods are mild, selectively removing mineral components without significantly altering the organic matter. The more drastic methods break down the coal structure, separating it into an inorganic sludge and an organic product essentially not coal. As a recently publicized example, high-gradient magnetic separation has been proposed as a technique for removing pyrite and other weakly paramagnetic minerals from slurried coal.¹ The Bureau of Mines' froth flotation process² removes pyrite and other minerals by taking advantage of differences in density and wettability of these undesirable substances and organic material. A method known as Meyer's Process³ involves up to six leaches of pulverized coal with ferric salt solution at about 100° C, converting pyrite to sulfate and elemental sulfur. A more vigorous chemical method⁴ requires leaching finely pulverized coal with aqueous alkali at about 225° C in a closed system under an inert atmosphere, followed by treatment with strong acid and leaching with water. The still more vigorous PAMCO process⁵ involves dissolution of coal in solvent at elevated temperature, hydrogen treatment, physical separation of undissolved matter, and vacuum distillation of the dissolved products.

Our laboratory is investigating methods for upgrading shale oil and high-sulfur coal by mild oxidation. Currently, experiments are being conducted with two types of oxidation systems--one using oxygen, which shows promise as a method for upgrading shale-oil distillates,⁶ and the other using mixtures of H₂O₂ and acid, which may be useful for upgrading both shale oil and coal. This report describes results of treating several high-sulfur coals with solutions of H₂O₂ in H₂SO₄, or with H₂SO₄ alone. Acid concentrations ranged from 0.1 N to 0.5 N, H₂O₂ concentrations ranged from 7 to 17 percent, and treating periods ranged from 1 to 72 hours. Most of the tests were conducted at ambient temperature, but in one test series, the solutions were warmed to speed up the reaction.

EXPERIMENTAL PROCEDURES

Coals and Sample Preparation

Five different high-sulfur, high-volatile bituminous coals, representing a wide range of sulfur contents, sulfur types, and ash contents, were obtained from the Pittsburgh Energy Research Center. These were (A) Pittsburgh Seam, St. Clairsville, Ohio; (B) Pittsburgh Seam, Pittsburgh, Pennsylvania; (C) Illinois No. 5 Bed; (D) Hastie, Iowa Bed; and (E) Ft. Scott, Oklahoma Bed. Each coal as received was first screened through a 32-mesh screen to separate fine and coarse material. The plus 32-mesh material was crushed in a ceramic mill jar with Burundum cylinders; that which passed through the 32-mesh screen was combined with the initially separated fine material, and the plus 32-mesh material was returned to the mill jar for further crushing. This process was repeated until the entire sample was reduced to minus 32 mesh.

Reagents and Analytical Procedures

Reagents

H_2O_2 (30 percent), H_2SO_4 , and HCl were ACS reagent grade. $\text{Ce}(\text{SO}_4)_2$ was certified 0.1000 N solution standardized against primary standard iron wire. Treating solutions were prepared by dilution based on label values.

Coal Analyses

Proximate and ultimate composition and heating values were determined by standard methods⁷ at the Bureau of Mines Coal Analysis Laboratory, Pittsburgh Energy Research Center.

Determination of Extracted Iron

An aliquot of filtered spent treating solution was transferred to a 125-ml Erlenmeyer flask, 2-ml 6 N H_2SO_4 was added, the mixture was heated to boiling, and 0.5 N KMnO_4 solution was added dropwise until the pink color persisted for at least 2 minutes. After addition of 10-ml of 6 N HCl , the solution was again brought to a boil, reduced by the Zimmerman-Reinhardt method, and titrated with 0.1 N cerate solution using Ferroin indicator. A blank titer was determined on the reagents, subtracted from the sample titers, and the net titers calculated as Fe.

Treating Procedures

Varying the Treating Time

Ten-gram samples of coal A were shaken at ambient temperature in 500-ml Pyrex Erlenmeyer flasks with 100-ml portions of solution, which were 17 weight-percent H_2O_2 and 0.3 N H_2SO_4 . Treating times were 2, 4, 19, 24, 48, and 72 hours. One sample was treated with 0.5 N H_2SO_4 alone for 72 hours. After treating, each mixture was filtered with the aid of vacuum through a fine-porosity fitted glass funnel, and the coal was washed several times with water until a small portion of wash showed little or no sulfate content. Each treated coal and a portion of the untreated coal were dried for 2 hours in a vacuum desiccator at 80° C and analyzed for proximate and ultimate composition and heating value. The combined filtrates and washes from each coal sample were analyzed for iron content.

Varying Hydrogen Peroxide Concentration

Thirty-gram samples of coal A were treated for 2 hours in the manner previously described with 100-ml portions of solution, each 0.1 N in H_2SO_4 but with different concentrations of H_2O_2 in each. Hydrogen peroxide concentrations were 7, 9, 11, 13, 15, and 17 percent. After filtering and washing, the coals were dried and analyzed, and the extracted iron was determined in each filtrate.

Treating Coals Containing Different Proportions of Inorganic and Organic Sulfur

Coals B, C, D, and E, ranging in pyrite sulfur content from less than 1 percent to more than 4 percent and ranging in organic sulfur content from 1 percent to 3 percent, were treated for 1 hour with 15 percent H_2O_2 solutions that were 0.3 N H_2SO_4 and with 0.3 N H_2SO_4 alone. The volume of treating solution was 250-ml and the sample weight was 50 grams in each test. The treating and workup procedures were the same as previously described.

Repetitive Treating

Coals B and C were treated with 250-ml portions of 0.3 N H_2SO_4 -10 percent hydrogen peroxide as follows: Three 50-gram samples of each coal were first treated as previously described for 1 hour at ambient temperature. After filtering the three mixtures, one sample was worked up for analysis, and the other two were retreated with fresh solution for 3 hours at 55° C. After filtering the remaining two, one was worked up for analysis; the last sample was treated a third time with fresh solution for 7 hours at 85° C., filtered, and worked up for analysis.

RESULTS AND DISCUSSION

Analyses of samples of coal A before and after treating for 2 to 72 hours are shown in table 1. Acid-peroxide treatment caused a 49-percent decrease in sulfur content and a 32-percent

TABLE 1. - Results¹ of treating high-sulfur coal A with H_2O_2 - H_2SO_4 or with H_2SO_4 alone

Treating time, hr	Treating solution ²		C	H	N	S	O	Ash	Heating value, Btu/lb	Extracted Fe, wt-pct of coal
	H_2O_2 , wt-pct	H_2SO_4 , N								
Untreated coal			68.9	4.8	1.1	4.5	7.9	12.8	12,460	0
2	17	0.3	74.8	5.0	1.3	2.3	7.8	8.7	---	1.92
4	17	.3	75.2	5.0	1.3	2.0	7.9	8.6	---	2.27
19	17	.3	75.4	5.0	1.3	1.9	8.4	8.0	13,310	2.32
24	17	.3	75.1	4.9	1.3	2.0	8.3	8.4	---	2.33
48	17	.3	75.0	5.0	1.3	2.0	8.5	8.2	---	2.39
72	17	.3	74.8	5.0	1.3	2.0	9.0	7.9	13,380	2.45
72	0	.5	72.3	4.8	1.2	3.9	7.5	10.8	12,890	.31

¹ Ultimate analyses and heating values on a dry basis.

² 100-ml solution per 10 grams of minus 32-mesh coal, ambient temperature.

decrease in ash content in 2 hours; thereafter, sulfur and ash contents decreased slowly to minimums of 44 and 62 percent, respectively, of original values. Values of iron extracted followed a similar trend, which indicated that most improvements in composition were substantially accomplished in 2 to 4 hours. Heating values of the treated samples were about 7 percent higher than that of the untreated coal. The sample treated for 72 hours with 0.5 N H_2SO_4 alone showed a modest increase of 3.5 percent in heating value and decreases of only 13 percent in sulfur and 16 percent in ash. It is apparent that this treatment for 72 hours had less effect on the coal than 2 hours of treatment with acid-peroxide, which demonstrates the importance of H_2O_2 in the solution.

Another series of tests on the same coal indicates the importance of sulfuric acid in the treating solution. In these tests conducted for 2 hours at ambient temperature, the initial concentrations of hydrogen peroxide were varied from 7 to 17 percent; initial sulfuric acid concentration was 0.1 N in each solution. The results, shown in table 2, show that at peroxide concentrations greater than 7 percent, very little further change in coal composition was achieved. At 17 percent peroxide concentration, comparison of these results with the results of 2 hours treating shown in table 1 indicate that the solution with the higher acid concentration was more effective in removing iron and sulfur and in lowering ash content. The analyses of sulfur forms show that only mineral sulfur was affected by acid-peroxide under these conditions. Neither organic sulfur nor nitrogen contents were appreciably affected by these treatments, and the increased heating values indicate there was little or no attack on organic components.

TABLE 2. - Composition¹ of high-sulfur coal A before and after treating
with $\text{H}_2\text{O}_2\text{-H}_2\text{SO}_4$ solution

Treating H_2O_2 , wt-pct	Solution ² H_2SO_4 N	Ultimate analysis, wt-pct						Sulfur forms, wt-pct			Heating value, Btu/lb	Extracted Fe, wt-pct of coal
		C	H	N	S	O	Ash	SO_4	Pyr.	Org.		
Untreated coal		68.9	4.8	1.1	4.5	7.9	12.8	0.41	2.30	1.79	12,460	0
7	0.1	73.0	5.0	1.2	3.3	8.0	9.5	.06	1.44	1.80	13,150	1.15
9	.1	73.0	5.0	1.2	3.1	8.4	9.4	.06	1.22	1.82	13,160	1.37
11	.1	72.9	5.0	1.2	3.1	8.5	9.3	.01	1.31	1.78	13,130	1.31
13	.1	73.3	5.0	1.2	2.9	8.6	9.0	.05	1.12	1.73	13,180	1.39
15	.1	73.3	5.1	1.2	2.8	8.3	9.3	.08	.94	1.78	13,170	1.41
17	.1	73.3	5.0	1.2	2.9	8.4	9.2	.09	1.04	1.77	13,200	1.50

¹ Ultimate analyses and heating values on a dry basis.

² 200-ml solution per 30 grams of minus 32-mesh coal, 2 hours at ambient temperature.

To test the effectiveness of acid-peroxide treatment on coals having widely different proportions of sulfur types, 50-gram samples of four coals were treated for 1 hour at ambient temperature with 250-ml volumes of either 15 percent $\text{H}_2\text{O}_2\text{-}0.3\text{ N H}_2\text{SO}_4$ or $0.3\text{ N H}_2\text{SO}_4$ alone. Results are shown in table 3. In all cases acid-peroxide treatment was more effective than treatment with acid alone in terms of reducing sulfur and ash contents and increasing heating values. As previously observed, only the sulfate and pyrite sulfur were removed. Treatment of coal C with $0.3\text{ N H}_2\text{SO}_4$ removed iron equivalent to 2 weight-percent of the sample, the source of which was not pyrite. Calculated as iron oxide, this amount of iron would account for the difference in ash content in this acid-washed sample and the untreated coal. In general, dilute sulfuric acid treating removed varying amounts of mineral matter, including sulfates and nonpyrite iron, but had no apparent effect on pyrite. In every case, acid-peroxide solution removed more mineral than acid alone and removed most of the pyrite but had no apparent effect on organic matter under these mild conditions.

To test the effects of multiple treatments, 50-gram samples of coals B and C were treated with one, two, or three 250-ml portions of a solution which was 10 weight-percent H_2O_2 in $0.3\text{ N H}_2\text{SO}_4$. Reactions in second and third treatments were quite slow at ambient temperature, and the flasks were warmed to expedite peroxide decomposition. Analyses of the treated samples and of the untreated coals are shown in table 4 and show that these coals suffered some loss in quality when treated for a second and third time, characterized by a trend toward lower carbon contents and heating values accompanied by rising oxygen and ash contents. Even though the pyrite contents of the coals had decreased after the third treatment to less than 10 percent of the original contents, the amounts removed by repeated treatment were relatively small. Both coals show a modest decrease in organic sulfur content after treating a second and third time. The change in coal C is more significant, amounting to a decline of 11 percent of the organic sulfur present in the coal after the first treatment. The results indicate that continued exposure to acid-peroxide after pyrite or other reactive minerals are removed leads to oxidative attack on the organic matter.

Although the main object of these experiments was to gauge the potential of a strongly oxidizing system for demineralizing coal, rather than to examine the chemistry in detail, some observations of mainly chemical interest emerged. Treatment of the coals used in this work with 10 to 15 percent H_2O_2 solution for 1 to 2 hours at ambient temperature had very little effect on coal composition. The foregoing experiments demonstrate that in the concentrations employed, only the mixture of H_2O_2 and H_2SO_4 , but neither reagent alone, is capable of attacking pyrite or

TABLE 3. - Analyses¹ of coals before and after treating with $\text{H}_2\text{O}_2\text{-H}_2\text{SO}_4$ or with H_2SO_4 alone

Coal	Treating solution ²		Ultimate analysis, wt-pct						Sulfur forms, wt-pct			Heating value, Btu/lb	Extracted Fe, wt-pct of coal
	wt-pct	H_2O_2 , H_2SO_4 , N	C	H	N	S	O	Ash	SO_4	Pyr.	Org.		
B	Untreated coal		71.8	5.1	1.4	1.8	8.2	11.7	0.06	0.74	1.00	12,990	0
	0	0.3	72.3	5.0	1.4	1.8	8.0	11.5	.04	.79	.97	12,960	0.04
	15	.3	73.5	5.0	1.4	1.1	8.2	10.8	.02	.08	1.00	13,060	.63
C	Untreated coal		69.8	4.7	1.3	3.6	11.0	9.6	.08	1.06	2.46	12,590	0
	0	.3	71.5	4.9	1.3	3.6	10.1	8.6	.01	1.11	2.48	12,800	.08
	15	.3	72.0	5.0	1.3	2.7	11.5	7.5	.06	.09	2.55	12,860	1.02
D	Untreated coal		58.7	4.6	1.0	8.7	9.9	17.1	2.00	3.93	2.77	10,700	0
	0	.3	65.7	4.9	1.1	7.9	6.5	13.9	.51	4.45	2.94	11,900	2.06
	15	.3	68.9	5.1	1.2	4.4	10.8	9.6	.29	1.15	2.96	12,360	4.38
E	Untreated coal		73.7	5.3	1.6	4.1	6.7	8.6	.48	2.05	1.57	13,300	0
	0	.3	75.9	5.5	1.6	3.8	6.4	6.8	.07	1.94	1.79	13,770	.46
	15	.3	77.0	5.6	1.7	2.5	8.0	5.2	.04	.58	1.88	14,040	1.56

¹ Ultimate analyses and heating values on a dry basis.² 250-ml solution per 50 grams minus 32-mesh coal, ambient temperature for 1 hour.TABLE 4. - Effects of repeated treatment with 10-percent $\text{H}_2\text{O}_2\text{-0.3 N H}_2\text{SO}_4$ on the composition¹ of two high-sulfur coals

Coal	Total treatments ²	Ultimate analysis, wt-pct						Sulfur forms, wt-pct			Heating value, Btu/lb	Extracted Fe, wt-pct of coal
		C	H	N	S	O	Ash	SO_4	Pyr.	Org.		
B	Untreated	71.8	5.1	1.4	1.8	8.3	11.6	0.06	0.74	1.00	12,990	0
	1	73.3	5.1	1.4	1.2	8.2	10.8	.01	.11	1.08	13,090	0.60
	2	72.5	5.0	1.4	1.0	9.3	10.8	.0	.04	.96	12,980	.72
	3	71.5	5.0	1.4	1.0	9.9	11.2	.0	.03	.97	12,630	.74
A	Untreated	69.8	4.7	1.3	3.6	11.0	9.6	.08	1.06	2.46	12,600	0
	1	72.9	5.1	1.3	2.8	10.3	7.6	.06	.16	2.58	12,900	.84
	2	72.7	5.0	1.4	2.6	11.3	7.0	.08	.08	2.44	12,840	1.22
	3	70.1	4.6	1.3	2.5	14.3	7.2	.11	.10	2.29	12,240	1.14

¹ Ultimate analyses and heating values on a dry basis.² Each treatment 250-ml solution per 50 grams minus 32-mesh coal. First treatment, 1 hour at ambient temperature; second treatment, additional 3 hours at 55° C; third treatment, additional 7 hours at 85° C.

demineralizing coal to the extent observed. It is therefore reasonable to postulate that peroxysulfuric acid, H_2SO_5 , is formed in equilibrium quantity in the mixture and plays an important role in the reaction. However, the expected initial H_2SO_5 concentration would be extremely low in the solution employed in this work because of the low H_2SO_4 concentration and the low value of the equilibrium constant measured by Monger and Redlich.⁸ Further, in view of the rapid decomposition of H_2O_2 in contact with high-sulfur coal and the apparent low rate of H_2SO_5 formation,⁸ it is difficult to reconcile the amount of peroxyacid expected in the treating solutions with the amounts of pyrite and other minerals removed unless it is assumed that substances in coal catalyze peroxyacid formation. This catalytic effect has been observed for a number of metal ions and for sulfates,⁸ and so could be expected in mixtures of H_2O_2 , H_2SO_4 , and coal. The principle reactions are therefore visualized as catalytic formation of H_2SO_5 and oxidation of pyrite with competing peroxide decomposition by metal ions. After removal of most of the active metals and sulfates from coal, oxidative attack on the organic matter becomes significant as indicated by analyses of coal subjected to repeated acid-peroxide treatment (table 4).

Evolution of small amounts of hydrogen sulfide was detected when coals were treated with acid-peroxide, although none was detected when using H_2SO_4 or H_2O_2 alone. Its presence in the strongly oxidizing media was surprising. Acid concentrations were apparently too low to produce H_2S from pyrite, in view of the selective extraction of sulfate from coal with $\sim 3 \text{ N HCl}$, which is not expected to attack pyrite.⁷ Nalwalk and coworkers⁹ report that decomposition of coal with 30 percent H_2O_2 slowly oxidized pyrite to sulfate, but no evolution of H_2S was mentioned either in this work or that of Ward.¹⁰ The formation of H_2S cannot be conveniently explained as a result of H_2SO_5 formation because it is apparently a weaker acid than sulfuric acid.⁸ However, the formation of H_2S in minute quantities, whatever the reaction path, is not expected to be important in the overall reaction.

Further experimentation is in progress to determine the most effective concentrations of peroxide and sulfuric acid for coal demineralization. On the premise that peroxysulfuric acid is the most effective reagent and in order to increase its initial concentration, the concentration of sulfuric acid must be considerably higher than used in the initial experiments described in this work.

CONCLUSIONS

Treatment of high-sulfur coals with H_2SO_4 - H_2O_2 solution lowers the sulfur and ash contents of the coals by removing pyrite, iron, and other minerals, leading to fuels of higher heating value. No significant attack on organic constituents occurs at ambient temperature before minerals susceptible to oxidation have been removed. Acid-peroxide treatment apparently has potential as a method for demineralizing high-sulfur coals.

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KEROGEN CONSTITUENTS: REDUCED CHLOROPHYLLIN AS A MODEL FOR THE PRECURSORS OF NITROGENOUS COMPOUNDS IN SHALE OIL

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INTRODUCTION

In evaluating and developing the resource potential of the Nation's vast oil-shale reserves, the U.S. Bureau of Mines has been conducting research in the origins and chemistry of shale oil. As part of this work, the role of plant pigments and their decomposition products as possible precursors of the nitrogenous compounds found in shale oil was investigated. An accurate picture of the origin of the compounds and their compound types may be an aid in analyzing the character of the oil, its suitability as a refinery feedstock, or perhaps its importance as a source of commercially valuable chemical compounds.

The idea that plant pigments may be the origin of nitrogen-containing compounds in shale oil is not new. Mapstone has proposed that the pyrroles found in shale oil result from the pyrolysis of the porphyrins in chlorophyll.¹ It has been shown that kerogen, the organic phase of oil shale, is 45 to 60 percent heterocyclic material.² This work was undertaken to substantiate Mapstone's proposal and to see if plant pigments could be the origin of the heterocyclic material in kerogen.

Experimentally, a comparison between the nitrogen compounds in a shale-oil light distillate and the nitrogenous compounds found in the pyrolysates of chlorophyll derivatives was made. The similarity of the compounds found in both the shale oil and chlorophyllin pyrolysate indicates that reduced chlorophyllin derivatives are a good model for the portion of kerogen that produces nitrogen compounds upon pyrolysis of oil shale. The present paper describes the preparation and characteristics of the kerogen model and shows that pyrolysis of this model yields pyrroles and products which are comparable to the nitrogenous products of shale oil.

EXPERIMENTAL PROCEDURE

Description of Materials

Commercial Chlorophyllin

Chlorophyllin is commercially available as the trisodium-copper salt with the empirical formula $C_{31}H_{31}N_4Cu(CO_2Na)_3$. Most processes for commercial production of chlorophyllin involve saponification of plant material, and the resulting product frequently contains fatty acid salts as impurities.³ A commercial sample of chlorophyllin with a nitrogen content of 4.83 percent was used in this study. This compares with the theoretical value of 7.73 for the pure salt, indicating that the commercial sample is 63 percent pure. The remaining material is assumed to be fatty acid salts.

Shale-Oil Light Distillate

Samples for mass spectral analysis were obtained as follows. A 110-g sample of an in situ shale-oil light distillate was separated on 880 g of Florisil. Each fraction was monitored by infrared spectroscopy as a 2-percent solution in carbon tetrachloride. The fraction richest in pyrrolic

N-H (as indicated by the intense band at $3,480\text{ cm}^{-1}$) was further fractionated into six subfractions, A_0 - A_5 , using the method of Snyder and Buell for separations on alumina.⁴ Three of the subfractions-- A_2 , A_3 , and A_5 --were sufficiently different in the IR to be examined individually by mass spectroscopy, along with two later fractions which gave indications in the infrared of meriting further study.

Reduction and Pyrolysis of Chlorophyllin

Reduction

The reduction of chlorophyllin with PtO_2 in glacial acetic acid with the resultant uptake of three moles of hydrogen to give hexahydrochlorophyllin is reported in the literature⁵ as a straightforward reaction, but this was not found to be so during the course of this study. Using a PtO_2 -to-chlorophyllin ratio of 2:25, H_2 pressure of 275 psig (at 25°C), and heating to 150°C for 72 hours resulted in only partial reduction. At no time during this study was the success of the reaction predictable. In each case the reduced platinum was removed by filtration, and the acetic acid was removed with mild heat and vacuum on a rotary evaporator. The resulting dark brown material was the synthetic kerogen which was pyrolyzed to yield the oils which were compared with shale oil. For additional comparison, a sample of commercial chlorophyllin was dissolved in acetic acid and then recovered by the above technique to yield chlorophyllin acetate for pyrolysis.

Pyrolysis of Reduced Chlorophyllin

Samples to be pyrolyzed ($\sim 10\text{ g}$) were placed in a 300-ml flask which was connected to a trap cooled with liquid nitrogen. The system was evacuated to $\sim 10^{-2}\text{ mm}$ for at least 30 minutes; then the pressure was reduced to $\sim 10^{-5}\text{ mm}$, and heat was applied to the sample container with a hot air bath. Heat was applied slowly, and as it approached 200°C a clear distillate began to collect in the trap. This was believed to be excess acetic acid and perhaps some water. The pressure in the system also took a rapid jump to $\sim 10^{-2}\text{ mm Hg}$ as CO_2 was eliminated from the acids present. After the pressure began to drop, additional heat was applied until the temperature in the air bath reached 375°C to 425°C . The temperature was maintained at this level until no more distillate, a dark red-brown liquid, was observed coming from the sample. At this point the pressure had risen to 10^{-2} mm Hg and remained fairly constant. The heating was discontinued, the system was allowed to cool to room temperature, and the pressure was returned to normal. The frozen distillate was dissolved in ethyl ether and washed with saturated NaHCO_3 until the wash water was basic. The sample was dried over anhydrous K_2CO_3 , and the ether was removed at room temperature under a slight negative pressure. If the acetic acid and water were not removed immediately, the sample tended to polymerize and form heavy precipitates. The samples were stored under a nitrogen atmosphere at 0°C .

Characterization Procedures

Chromatographic Separation and Analysis

The pyrolysates from chlorophyllin and a reduced chlorophyllin were treated with an ion-exchange resin to separate the basic from the neutral material in the following manner. Two ml of a 5-percent solution of the pyrolysate in cyclohexane were passed through a column containing 1.0 g of activated Rohm and Haas Amberlyst 15 cation-exchange resin with cyclohexane as the solvent. The first 2 ml of eluent were collected and used in the subsequent analysis. GC analysis by simulated distillation of aliquots of the solution before and after treatment and comparison of the sample areas gave percent basic nitrogen in the total sample. Breakdown of the GC output in terms of 50°C increments gives the relative distribution of compounds according to boiling range and, by inference, according to molecular weight.

Titrimetric Analysis

Titration of the bases in the pyrolysates was done in acetic anhydride and in acetonitrile using an autotitrator. The titrations were performed on samples containing about 0.1 milliequivalent of nitrogen, using 0.1 N perchloric acid in dioxane based on the methods of Wimer⁶ and Buell.⁷ The electrode system was glass versus calomel reference, and the electrolyte in the calomel electrode was methanolic KCl.

Infrared Analysis

Qualitative spectra of all fractions were run as 2-percent solutions in carbon tetrachloride with 0.5-mm NaCl cells. Quantitative pyrrolic N-H was determined by the method of Koros, et al.⁸

Mass Spectral Analysis

Low-ionizing voltage mass spectrometry at 14 to 16 nominal volts was used to obtain the molecular weights of the various homologous series in various samples. High-resolution spectra were run at 70 eV to confirm the empirical formulas of the various ions.

RESULTS AND DISCUSSION

Table 1 lists the elemental composition of the starting materials as well as the distillates

TABLE 1. - Elemental composition of the starting materials, distillates, and residues from the pyrolysis of some samples of chlorophyllin and its related products

Sample	Carbon, wt-pct	Hydrogen, wt-pct	Nitrogen, wt-pct	Carbon/hydrogen
Chlorophyllin	59.46	5.82	4.83	0.85
Distillate	85.31	9.31	5.18	.76
Residue	59.50	4.16	5.41	
Chlorophyllin acetate	58.45	6.14	4.26	.79
Distillate	85.31	9.78	4.49	.73
Residue	59.67	4.08	5.29	
Reduced chlorophyllin A ¹	60.07	6.53	2.88	.77
Distillate	85.21	10.90	2.96	.65
Residue	59.49	3.82	5.04	
Reduced chlorophyllin B ¹	46.24	6.03	2.19	.64
Distillate	80.85	10.00	4.78	.67
Residue	38.45	2.73	2.99	

¹ Reduced chlorophyllin A and B are products of two separate reductions of commercial chlorophyllin with PtO₂.

and residues from the pyrolysis of some samples of chlorophyllin and related products. The reduction caused some hydrodenitritification, as shown by the lowered nitrogen percentages. Upon pyrolysis, the two reduced materials gave the products with the lowest carbon-hydrogen ratio as would be expected.

Figure 1 shows the distribution of basic and neutral compounds as defined by their affinity for adsorption on Amberlyst 15 resin. Pyrolysis of reduced chlorophyllin produces 50 percent more basic material than does pyrolysis of the nonreduced material, and it is noteworthy that most of this additional material is fairly low boiling, falling in the 200 to 300° C range.

Titration of the pyrolysates in nonaqueous solvents gives information concerning the strength of the various bases present. These data are presented in table 2. There appears to be no correla-

TABLE 2. - Nitrogen composition of distillates

Distillate source	Titrateable N, total	Wt-pct strongly basic	Wt-pct weakly basic	Wt-pct very weakly basic
Chlorophyllin	1.52	0	0.78	0.74
Chlorophyllin acetate	1.68	0	1.22	.46
Reduced sample A	1.57	0	.76	.81
Reduced sample B	3.08	0	.82	2.25

tion between the amount of hydrogen in the starting material and the types of bases formed, but the presence of bound acetic acid does favor the production of weak bases at the expense of the very weak bases.

Tables 3 and 4 list the homologous series of nitrogen compounds found in the low-ionizing-voltage mass spectrum of the reduced chlorophyllin pyrolysate having the highest pyrrolic N-H content, 2.02 percent, and the five fractions of the shale-oil light distillate, respectively. High-resolution mass spectra on reduced chlorophyllin pyrolysates confirm the presence of all the mononitrogen series of compounds listed in table 3. In the shale-oil light distillate, the $Z = -3$ series is missing from the high-resolution mass spectrum. Its absence is unusual because pyrroles have been isolated from shale oil.⁹ The absence of the $Z = +1$ series in the mass spectrum of the pyrolysate is not too surprising; few materials in such a reduced state would be expected from the thermal decomposition of what is basically a hydrogen-poor substrate. The absence of the $Z = -7$ series in the reduced chlorophyllin pyrolysate cannot be explained at this time, but it has been found in other reduced chlorophyllin pyrolysates.

For the Z series (-3, -5, -7, -11) found in various chlorophyllin pyrolysates by mass spectrometry, the following compound types are probably represented: Pyrroles (-3); cycloalkylpyrroles, pyridines (-5); cycloalkylpyridines (-7); indoles (-9); and azanaphthalene derivatives (-11). These represent materials whose presence has been reported in shale oil before^{9,10} or that were found in this work. It is felt, therefore, that chlorophyllin derivatives, especially the reduced materials, represent a reasonable model for the portion of kerogen that produces nitrogen-containing compounds upon pyrolysis.

SUMMARY

The reduction and pyrolysis of a commercially available plant pigment extract, chlorophyllin, is described. The amounts of bases formed and their boiling-range distribution are related to the hydrogen content of the starting materials. Mass spectral studies are given which show that many of the same types of bases are found in the pyrolysate and in an in situ light distillate. These results indicate that reduced chlorophyllin may be used as a model for the nitrogen-containing constituents in kerogen.

TABLE 3. - Mononitrogen-containing molecular ions in the low-ionizing voltage mass spectrum of reduced chlorophyllin pyrolysate

Series	General formula	Carbon No. range	Rings plus double bonds
I-a	$C_nH_{2n-3}N$	6-14	3
I-b	$C_nH_{2n-5}N$	7-15	4
I-c	$C_nH_{2n-9}N$	10-15	6
I-d	$C_nH_{2n-11}N$	14-18	7

TABLE 4. - Nonnitrogen-containing molecular ions from the low-ionizing voltage mass spectra of chromatographic fractions of shale-oil light distillate

Series	General formula	Carbon No. range	Rings plus double bonds
<u>Fraction A₂</u>			
II-a	$C_nH_{2n+1}N$	8-14	1
II-b	$C_nH_{2n-11}N$	10-13	7
II-c	$C_nH_{2n-9}N$	10-14	6
<u>Fraction A₃</u>			
II-d	$C_nH_{2n-11}N$	9-14	7
<u>Fraction A₅</u>			
II-f	$C_nH_{2n-7}N$	8-12	5
II-g	$C_nH_{2n-9}N$	12-15	7
<u>Fraction 42</u>			
II-h	$C_nH_{2n-9}N$	8-12	6
II-i	$C_nH_{2n-11}N$	11-15	7
II-j	$C_nH_{2n-13}N$	13-15	8
<u>Fraction 58</u>			
II-k	$C_nH_{2n-5}N$	8-15	4
II-l	$C_nH_{2n-11}N$	9-14	7

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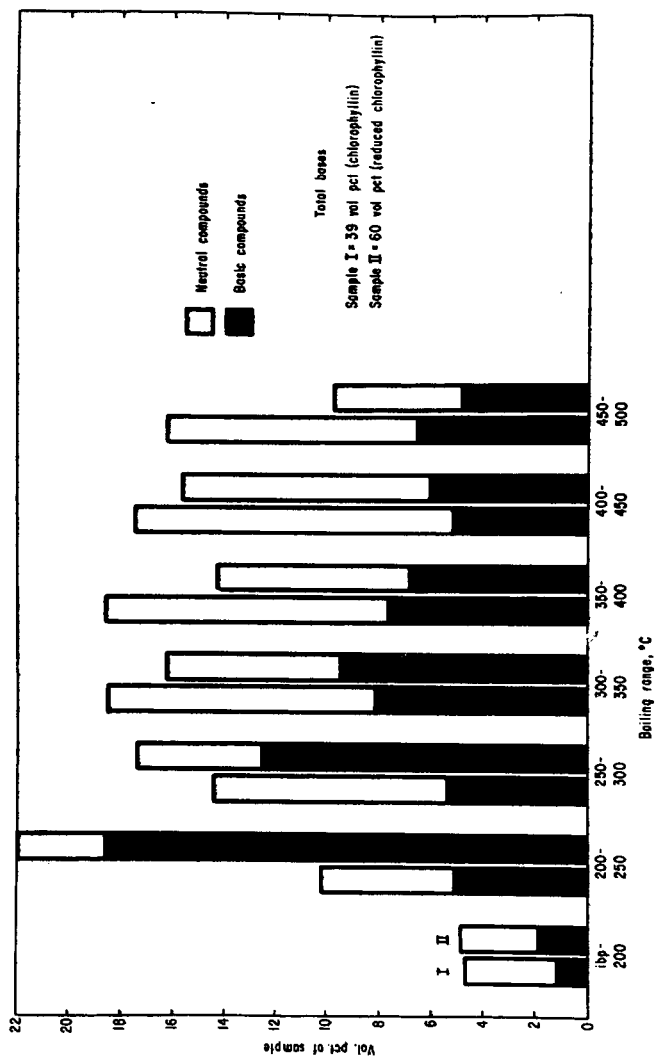


FIGURE 1. - Distribution of compounds in distillates.

NITROGEN COMPOUND TYPES IN GREEN RIVER OIL SHALE AND ITS KEROGEN DEGRADATION PRODUCTS

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INTRODUCTION

Information about the nitrogen compounds in oil shale and oil-shale degradation products is needed in order to provide more efficient processes for converting oil shale to useful energy with minimum environmental contamination. At present very little is known about the types of nitrogen compounds present in the soluble extracts that can be obtained from oil shale or the types of nitrogen compounds that are formed when previously extracted oil-shale samples are heated for prolonged periods at temperatures below those usually employed in retorting.

Some research has been done on the nitrogen compounds in shale oil and oil shale. Smith and coworkers¹ separated a shale-oil distillate boiling above 400° F on Florisil into hydrocarbon and nonhydrocarbon nitrogen-containing fractions. Haines and coworkers² published techniques for separating and identifying nitrogen compounds in petroleum and shale oil. Decora and Dinneen⁴ developed a gas-liquid chromatography method, based on using detergent as the solid phase, for separating basic nitrogen compounds in shale oil. Dinneen⁵ identified pyridines, indoles, quinolines, and tetrahydroquinolines in shale oil. Moore and Dunning⁶ isolated the porphyrins from oil-shale extracts and determined that they were complexed with iron and nickel. Anders and Robinson¹ studied the polar constituents isolated from Green River oil shale and found that alkoxy-pyrrolines, alkylmaleimides, tetrahydroquinolines, and quinolines were present in the polar material. Morandi and Jensen⁹ compared the porphyrins from a shale-oil fraction, oil-shale extract, and a petroleum fraction. They found that the porphyrins in oil shale are a complex mixture of etio-type porphyrins in the 366 to 522 molecular-weight range. Simoniet and coworkers¹³ studied nitrogenous compounds of the Green River Formation and found quinoline, indole or pyridine, and tetrahydroquinoline present in their oil-shale extracts.

The object of this research was to increase our knowledge about the effect of depth of burial on the nitrogen compounds present in Green River oil shale and to determine what types of nitrogen compounds are formed when oil shale is heated at temperatures in the range of 150° to 350° C for periods from 0.5 to 360 days. The present paper describes the results obtained for nitrogen compound-type analysis of fractions of the complex high-molecular-weight oil-shale products. In the study of extracts from the oil-shale core samples, an attempt was made to relate the analytical data to depth of burial and to determine if depth of burial affects the type of nitrogen compounds present in the extracts. In addition, the effect on oil-shale nitrogen structures due to long-time heating at low temperatures similar to that experienced peripherally to in situ retorting operations was determined.

EXPERIMENTAL PROCEDURES

The samples used in this study were obtained from two previous oil-shale studies. The extracts (soluble bitumen) obtained from a core of the Green River Formation are the same as described in a report by Robinson and Cook¹² on the 2,300-foot Colorado No. 1 core. The low-temperature thermal products (pyrolytic bitumen) are the same as those described by Cummins and Robinson³ where previously extracted 66-gpt oil shale from the Bureau of Mines' demonstration

mine at Rifle, Colorado was heated at temperatures ranging from 150° to 350° C for periods ranging from 0.5 to 360 days. The samples were fractionated into acid, bases, neutral-nitrogen, aromatic, and saturate compounds by a fractionation scheme. Each of the various fractions were analyzed for strong bases, weak bases, very weak bases, and nontitratable nitrogen by potentiometric titration. No attempt was made to distinguish between titratable nitrogen compounds and titratable nonnitrogen compounds; however, the latter type has been found by Poulson¹¹ to be insignificant in shale-oil products.

Product Fractionation

The samples used in this study are high-molecular-weight complex materials; however, they are amenable to a fractionation and separation scheme devised by Jewell, et al.⁷ Figure 1 shows the fractionation scheme used and the fractions that resulted.

The acid and base fractions are removed with Amberlyst A-29 anion- and Amberlyst 15 cation-exchange resins, while the neutral nitrogen fraction is removed by coordination-complex formation with ferric chloride supported on Attapulugus clay. Most of the nitrogen compounds are removed as acid, base, and neutral nitrogen fractions. The remaining hydrocarbon material was separated into aromatic and saturate fractions by adsorption chromatography on a column of Davison grade 12 silica gel.

Analyses of Fractions

The concentration of nitrogen present in the original samples and in the acid, base, neutral nitrogen, aromatic, and saturate fractions of these samples was determined using a system consisting of a reductive-nickel pyrolysis tube which directed the pyrolyzed product to an ammonia micro-coulometer. Samples were introduced through a boat inlet into the pyrolysis tube. Types of nitrogen compounds present in the fractions were determined using published methods by Streuli¹⁵ and Nicksic.¹⁰ No attempt was made to identify individual nitrogen compounds in this research. Nitrogen compounds referred to in this report are based on Buell's² published classification results.

RESULTS AND DISCUSSION

The nitrogen content was determined for samples obtained either by extracting portions of Colorado No. 1 core or by thermally degrading oil-shale kerogen. The nitrogen content of the oil-shale core extracts range from 0.11 to 0.82 percent, and the thermal degradation products ranged from 1.36 to 2.22 percent. On an average basis, the thermal product contains 2.7 times more nitrogen than the core extracts.

The distribution of the fractions obtained from Colorado No. 1 core extracts is shown in table 1. All the fractions contain more hydrocarbon (aromatic plus saturated) material than polar (acid, base, and neutral nitrogen) material except sample No. 7. The base-to-acid ratio remains at about one except for samples Nos. 24, 58, and 59. The base-to-neutral nitrogen ratio remains at about one except for samples Nos. 7, 24, and 58. The highest ratio of base-to-acid or base-to-neutral occurs in sample No. 58. The most hydrocarbons appear in the two samples at the bottom of the core. This generalization agrees with the results published by Robinson and Cook.¹² The average percents show that the polar materials are equally divided between the acid, base, and neutral nitrogen fractions. The various amounts of loss are probably complex high-molecular-weight materials generally insoluble in the solvents used in the fractionation scheme.

The distribution of fractions of kerogen thermal degradation products appears in table 2. The amount of aromatic and saturate fractions range from 37.7 to 60.0 percent of the total thermal

TABLE 1. - Distribution of the fractions obtained from Colorado No. 1 core extracts

Sample No.	Depth of burial, ft	Fraction, weight percent of total product					
		Acid	Base	Neutral-N	Aromatic	Saturate	Loss
5	943.7- 947.4	12.0	12.0	13.2	22.0	33.2	7.6
6	989.5- 990.5	11.7	10.5	9.3	22.1	30.7	15.7
7	995.4- 998.1	21.1	16.9	10.3	19.4	23.6	8.7
9	1,076.3-1,079.9	13.2	12.6	10.2	24.4	30.3	9.3
17	1,399.8-1,401.3	11.3	11.1	10.4	29.3	27.7	10.2
20	1,539.5-1,541.0	14.9	11.6	11.1	26.2	36.1	.1
24	1,696.1-1,697.1	6.0	10.8	23.1	29.3	23.2	7.6
58	3,039.0-3,040.3	4.2	12.8	7.0	20.2	40.6	15.2
59	3,065.1-3,071.2	2.3	4.8	5.8	17.9	66.8	2.4
Average		10.7	11.5	11.2	23.4	34.7	8.5

TABLE 2. - Distribution of fractions of kerogen thermal degradation products

Heating time, days	Temperature °C	Fraction, weight percent of total product					
		Acid	Base	Neutral-N	Aromatic	Saturate	Loss
360	150	12.4	15.4	17.0	21.2	16.5	17.5
90	200	7.9	11.3	10.6	25.5	27.9	16.8
12	250	17.2	21.2	7.1	24.3	19.6	10.6
4	300	8.3	23.2	6.3	34.0	26.0	2.2
0.5	350	9.1	25.3	15.7	34.4	7.5	8.0
Average		11.0	19.3	11.3	27.9	19.5	11.0

product. Three fractions contain less than 50 percent hydrocarbon material (aromatic and saturate). All the thermal products contain higher proportions of base than acid material. On an average basis, about the same amounts of acid and neutral material are present. The amount of aromatic material generally increases with temperature from 150° to 350° C and on an average is about 1.4 times the amount of either the saturate or base material. The percent loss tends to decrease with increased temperature as the complex materials are thermally degraded to lower-molecular-weight and more soluble materials.

The nitrogen content of fractions of the core extracts appears in table 3. As expected, most of the nitrogen is concentrated in the polar fractions, and the largest amount of nitrogen always appears in the base fraction. Samples Nos. 58 and 59 have base-to-acid nitrogen ratios ranging from 7 to 9.5 compared to an average of about 1.9 for samples 5 through 24. Also, samples Nos. 58 and 59 have base-to-neutral nitrogen ratios of 7 to 15 compared to an average of about 3 for samples Nos. 5 through 24. These results suggest some form of diagenetic process at the bottom of the core similar to that expected by thermal alteration.

Nitrogen content of fractions of the kerogen thermal degradation products appears in table 4. Most of the nitrogen appears in the base fractions as it did in the oil-shale core extracts. On an average basis, aromatic fractions contain about 2.5 times more nitrogen than the comparable core fraction while the saturate fractions are approximately equal. The ratios of nitrogen in the base fractions relative to the acid and neutral nitrogen for thermal products prepared at 200° C and above are high. They range from about 5 to 10 in regard to base-to-acid nitrogen ratio and

TABLE 3. - Nitrogen content of fractions of the core extracts

Sample No.	Nitrogen content, weight percent of total nitrogen					
	Acid	Base	Neutral-N	Aromatic	Saturate	Loss
5	25.8	42.8	15.0	4.5	3.4	8.5
6	23.2	39.7	13.9	2.9	3.2	17.1
7	19.8	40.6	10.9	1.9	1.2	25.6
9	24.7	55.8	11.1	3.4	3.1	1.9
17	22.1	42.8	20.0	5.0	3.5	6.6
20	24.8	29.7	19.2	6.6	4.6	15.1
24	12.4	38.7	8.5	5.6	5.6	29.2
58	5.1	48.7	3.3	9.6	13.9	19.4
59	9.0	63.6	9.0	9.0	9.0	.4
Average	18.5	44.7	12.3	5.4	5.3	13.8

TABLE 4. - Nitrogen content of fractions of the kerogen thermal degradation products

Heating time, days	Temperature °C	Nitrogen content, weight percent of total nitrogen					
		Acid	Base	Neutral-N	Aromatic	Saturate	Loss
360	150	14.9	26.7	6.2	4.3	2.5	45.4
90	200	7.0	33.6	9.9	9.6	5.5	34.4
12	250	15.4	46.0	7.1	10.2	5.4	15.9
4	300	2.7	26.7	4.1	12.2	7.2	47.1
0.5	350	5.6	38.0	9.8	25.4	3.6	17.6
Average		9.1	34.2	7.4	12.3	4.8	32.2

from about 3 to more than 6 for the base-to-neutral nitrogen ratio. These results are roughly similar to the results obtained on samples Nos. 58 and 59 of the core fractions (table 3) showing the change expected by thermal alteration.

The distribution of nitrogen-compound types present in fractions of the core extracts appears in table 5. Four different nitrogen-compound types were determined and are as follows: Strong bases, weak bases, very weak bases, and nontitratable nitrogen compounds. Contrary to what one would expect, strong base compounds appeared in the neutral nitrogen fractions. The separation method used should have retained any strong bases on the cation resins. One possible reason for the presence of strong bases in this fraction may be steric hindrance and molecular shape. Nitrogen compounds such as highly alkylated substituted pyridines could pass through the cation resin. No strong bases appear in any of the other fractions. All of the acid and base fractions contain both weak and very weak base type nitrogen compounds. Quinolines, hindered pyridines, and phenanthridines may be present in the weak-base type of nitrogen compounds. Weak bases are present in both the neutral nitrogen samples Nos. 6 and 17 and in saturate sample No. 9. All of the fractions except aromatic fraction No. 17 and saturate fractions Nos. 7 and 9 contain very weak base type nitrogen compounds. Very weak base type compounds could be anilines and certain acridines which acetylate and titrate as amides in acetic anhydride. All of the acid and aromatic fractions, three of the base fractions, one of the neutral nitrogen fractions, and two of the saturate fractions contain nontitratable nitrogen compounds. Nontitratable nitrogen-type compounds could be certain multiring pyrrolic nitrogen compounds, amides, or diamides that are partially or completely insoluble in acetic anhydride. Also, other high-molecular-weight insoluble materials in these fractions of the extracts could account for some of the titratable nitrogen type.

TABLE 5. - Distribution of nitrogen-compound types present in fractions of the core extracts

Sample No.	Nitrogen content, relative weight percent of total nitrogen			
	Strong base	Weak base	Very weak base	Nontitratable nitrogen
<u>Acid fraction</u>				
5	<1	4	6	90
6	<1	4	5	91
7	<1	4	5	91
9	<1	29	57	14
17	<1	46	46	8
<u>Base fraction</u>				
5	<1	6	6	88
6	<1	6	5	89
7	<1	5	4	91
9	<1	39	61	<1
17	<1	56	44	<1
<u>Neutral nitrogen fraction</u>				
5	33	<1	67	<1
6	<1	26	74	<1
7	14	<1	86	<1
9	32	<1	68	<1
17	<1	10	23	67
<u>Aromatic fraction</u>				
5	<1	<1	9	91
6	<1	<1	21	79
7	<1	<1	11	89
9	<1	<1	9	91
17	<1	<1	<1	100
<u>Saturate fraction</u>				
5	<1	<1	100	<1
6	<1	<1	100	<1
7	<1	<1	<1	100
9	<1	100	<1	<1
17	<1	<1	26	74

In general, the results show that most of the nitrogen compounds in the various fractions of the extracts from Colorado No. 1 core consisted of very weak bases or nontitratable nitrogen compounds. Some fractions contained weak bases and there was some evidence of strong bases in the neutral nitrogen fraction but generally the nitrogen components were of the less basic forms.

The distribution of nitrogen-compound types present in the kerogen thermal degradation products shown in table 6 are similar to that obtained for the core extracts in that most of the nitrogen-type compounds in the acid and base fractions appear in the weak base and very weak base class. Only the 360-day, 150° C saturate fraction contained strong base nitrogen compounds. This material must consist of high-molecular-weight hindered nitrogen compounds that did not react with the resins or with the silica-gel during the separation. Most of the nitrogen-type compounds in the neutral nitrogen fractions appear as nontitratable nitrogen; however, about half of the nitrogen in the 90-day, 200° C sample is very weak base type nitrogen as would be expected

TABLE 6. - Distribution of nitrogen-compound types present in fractions of the kerogen thermal degradation products

Heating time, days	Temperature, °C	Nitrogen content, relative weight percent of total nitrogen			
		Strong base	Weak base	Very weak base	Nontitratable nitrogen
<u>Acid fraction</u>					
360	150	< 1	35	65	< 1
90	200	< 1	51	29	20
<u>Base fraction</u>					
360	150	< 1	44	56	< 1
90	200	< 1	71	29	< 1
<u>Neutral nitrogen fraction</u>					
360	150	< 1	16	< 1	84
90	200	< 1	< 1	46	54
<u>Aromatic fraction</u>					
360	150	< 1	< 1	5	95
90	200	< 1	< 1	80	20
<u>Saturate fraction</u>					
360	150	62	< 1	< 1	38
90	200	< 1	< 1	9	91

by our separation scheme. One aromatic fraction contained 80 percent very weak base nitrogen compounds and two aromatic fractions contained more than 90 percent nontitratable nitrogen-type compounds.

In general, the results for the kerogen thermal degradation product were about the same as those obtained for the extracts from the oil-shale core samples. Most of the nitrogen compounds consisted of very weak bases or nontitratable nitrogen compounds; however, weak bases predominate in two of the fractions. One saturate fraction contained predominantly strong base; but, in general, most nitrogen compounds were of the less basic forms.

SUMMARY

Most of the nitrogen compounds in the extracts from oil-shale core samples and in the kerogen thermal degradation products consisted of very weak bases or nontitratable nitrogen. There was some evidence of strong bases and weak bases in some of the fractions, but generally the nitrogen-compound types consisted of the less basic forms. Basic nitrogen components were the most extensive at the greatest depth of burial for the core extracts, suggesting alteration to more basic forms of nitrogen compounds similar to those found in shale-oil products. The results of nitrogen-compound type analysis for the kerogen thermal degradation products prepared at 150° and 200° C were about the same as those obtained from extracts from the oil-shale core samples. Additional analyses will have to be made in order to determine the effect of increased temperature upon the nitrogen compound-type distribution.

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Reference to specific trade names does not imply endorsement by the Bureau of Mines.

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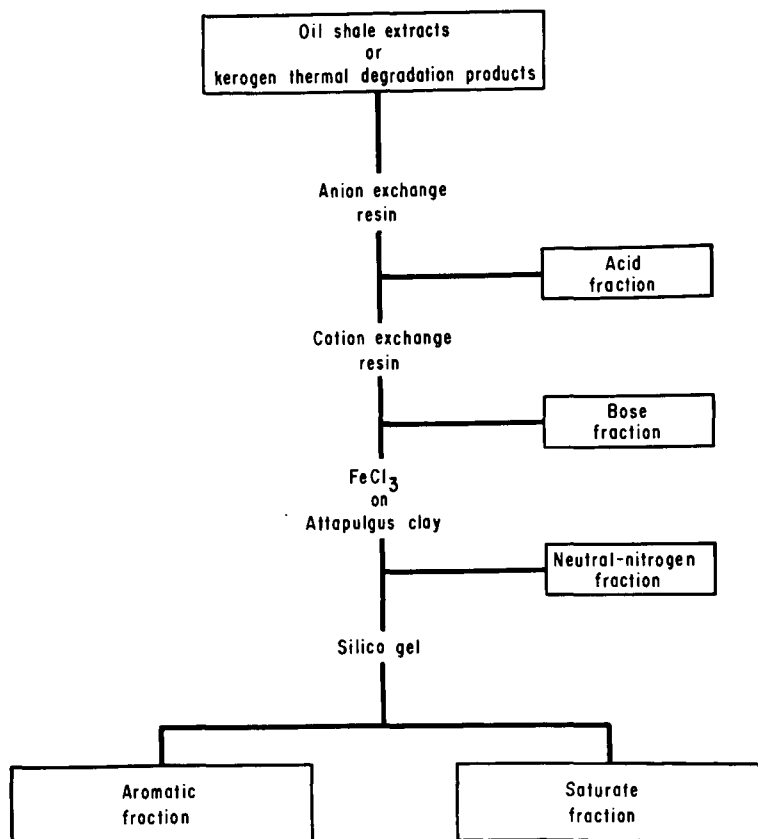


FIGURE I.-Fractionation scheme.

NITROGEN TYPES IN LIGHT DISTILLATES FROM ABOVEGROUND AND IN SITU COMBUSTION PRODUCED SHALE OILS

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INTRODUCTION

There is some evidence that in situ retorted shale oils may have generally lower heteroatom and polar compound concentrations than aboveground retorted oils.^{1,2} This could make in situ oils more attractive as refinery feedstock or as fuel sources than aboveground produced oils. To help determine if differences in heterocompound composition might exist between oils produced in these different ways, light distillate fractions (400° to 600° F nominal boiling range) from two different types of internal combustion retorting processes, one aboveground and one in situ, were compared in analyses. Both oils were produced in forward-burn type processes in which the exiting oil had the opportunity for contacting raw oil shale or included minerals.

The main difference in the two retorting processes was the time-temperature history of the oils produced. The aboveground process using crushed shale was a rapid-heat, high temperature process whereas the in situ process was apparently a slow-heat, low temperature process.¹ Direct gas-to-solids heat exchange occurs in both processes. Other imponderables such as the contact of the product oil with raw shale or air in either case, or raw or spent shale in situ could, of course, affect the character of the oil also.

The aboveground retorted oil (AGRO) was made from a shale oil produced from Colorado Green River Formation oil shale by the Union Oil Retort A³ and its nitrogen bases have been studied before.⁴

Additional compound-type information is available from early work with a shale-oil naphtha⁵ and a heavy gas oil⁶ from a different aboveground combustion retort-produced crude (a Nevada-Texas-Utah type retort). Much of this compound-type information has been drawn upon in the following discussion when specific compound types are postulated as relating to a nitrogen- or oxygen-type value determined.

The in situ retorted oil (ISRO) studied here was made from a shale oil produced in the Northern Green River Formation near Rock Springs, Wyoming.⁷ The shale used in the aboveground retort came from the Mahogany zone of the Piceance Basin in Colorado. Although the oil shales used were far apart, they were both of the Green River Formation. The Wyoming shale appears to be very similar in composition and properties to the extensively studied Mahogany zone oil shales.⁸ Therefore, it was assumed that if both shales had been retorted in the same way, the oils produced would have been similar.

The light distillate from the aboveground retorted oil (AGRO) represents 15 percent of the crude, but the light distillate from the in situ retorted oil (ISRO) represents 50 percent of the crude. A larger proportion of light products appears to be characteristic of in situ-produced shale oils.¹ In table 1 the heteroatomic concentrations are shown for the two distillates. Both oils have similar nitrogen levels, but sulfur and oxygen are much lower in the ISRO. The nature of sulfur and oxygen compounds in shale oils has been summarized earlier⁹ and in this symposium.² For production of refined products, sulfur and oxygen compound types apparently disappear with

hydrodenitrogenation before nitrogen types so that the nitrogen-type assessment seems of primary importance. For other contemplated uses of the resource, such as low grade burner fuel or as a source of specific chemical compounds, other heteroatomic compounds could be of comparable importance.

TABLE 1. - Heteroatoms in the shale-oil light distillates (400° to 600° F)

Element	Aboveground retorted oil	In situ retorted oil
	A	B
Total nitrogen	1.34	1.34
Sulfur	.90	.53
Oxygen (by difference in ultimate analysis)	1.24	.35

The weight-average molecular weight for the oils corresponds to $C_{14.3}$ or 200 based on simulated distillation. Using this value and assuming, for illustration, a maximum of heterocompounds with one nitrogen atom per molecule, the nitrogen levels shown in table 1 would represent 20 percent nitrogen-type compounds in either distillate. With similar assumptions for oxygen and sulfur, the AGRO would contain about 16 percent oxygen compounds and 6 percent sulfur compounds. The ISRO distillate would contain about 4 percent oxygen compounds and 3 percent sulfur compounds. Over 80 percent of the nitrogen in either of these oils is titratable as basic compounds.

This paper reports a comparison of some observed nitrogen types in these two oils (distillates). In addition, some oxygen types have been estimated because they appear to relate closely to the chemistry of the nitrogen types and there is a large difference in the elemental oxygen contents of the oils. Techniques for nitrogen-type characterization of shale oils developed and applied previously^{4,10} have been used. Some techniques in a state of development for phenolic and carboxylic acid-type characterization of shale oils have been applied also.

EXPERIMENTAL WORK

Separation Procedure

The fractionation scheme used is depicted in detail in figure 1 and summarized in table 2. The procedure¹¹ involved anion-exchange fractionation followed by cation-exchange fractionation to prepare three acid fractions (A_1 , A_2 , A_3) and three base fractions (B_1 , B_2 , B_3). The raffinate from this procedure was further fractionated on a ferric chloride-Attapulugus clay column¹¹ into three fractions (N_0 , N_1 , and N_2). The first of these neutral fractions, N_0 , is referred to also as the HC (hydrocarbon) fraction. Approximately 50 g of each distillate was fractionated using 50 g of each ion-exchange resin. Twenty grams of the raffinate from the ion-exchange resins was separated on 140 g of the ferric chloride-Attapulugus clay mixture.

The solvents were percolated at 20° C through the column removing most of the material in the fraction. The remaining amount of material was removed by percolating fresh solvent through the column and recirculating by distillation the solvent from the receiver back to the top of the column. Percolation was continued until there was no evidence of sample being desorbed from the column. Solvents were removed at reduced pressure, with slight rectification, and the recovered fractions were stored under an inert atmosphere at 0° C.

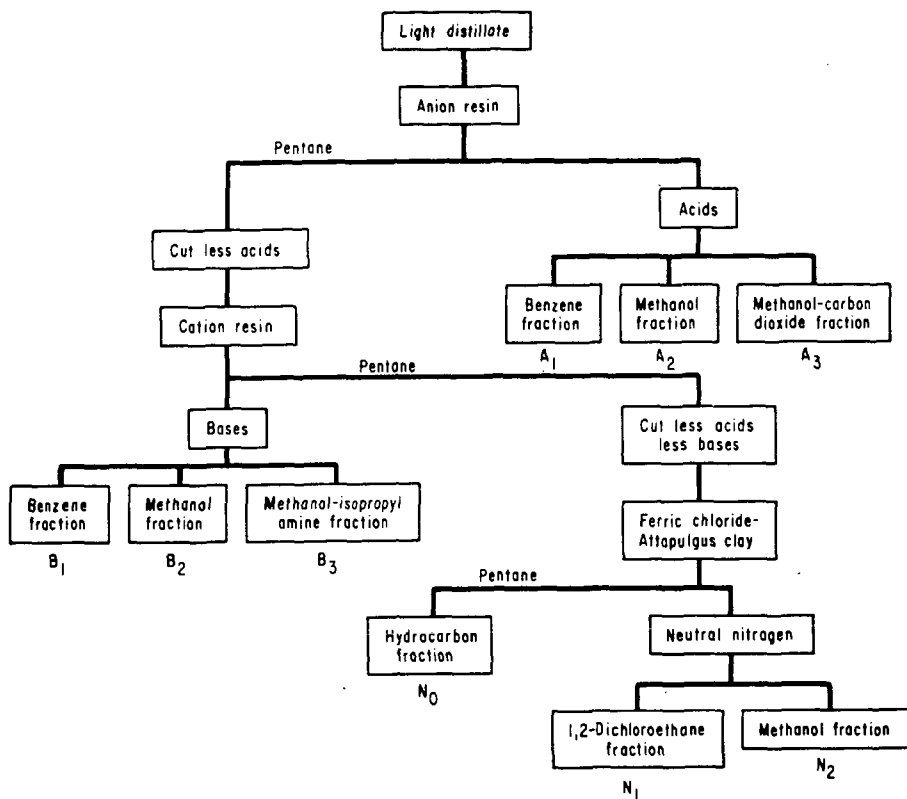


FIGURE 1. - Separation scheme.

Reagents

Adsorbents

The anion- and cation-exchange resins were Rohm and Haas Amberlyst A-29 and Amberlyst A-15, respectively. The resins and ferric chloride supported on clay were prepared, activated, and extracted as described by Jewell.¹¹

Solvents

N-pentane (99 percent, Phillips Petroleum) was purified by percolation through activated silica gel and by flash distillation. Benzene and methanol (reagent grade, J. T. Baker) were flash distilled as was 1,2-dichloroethane (Eastman Chemical Co.). The isopropyl amine (reagent grade, Eastman) was used as received. Acetonitrile and dioxane used in the titrations were purified by passing through activated alumina.

TABLE 2. - Anion-, cation-exchange, and ferric chloride-Attapulgius clay fractionation sequence

Fraction name	Desorbing solvent	Amount, wt-pct of distillate	
		Aboveground combustion retorted oil ^a	In situ combustion retorted oil ^b
<u>Acids From Anion-Exchange</u>			
<u>Resin Column</u>			
A ₁ , very weak	Benzene	1.65	1.32
A ₂ , very weak	Methanol	1.60	1.87
A ₃ , weak	Methanol-carbon dioxide	1.32	.76
<u>Bases From Cation-Exchange</u>			
<u>Resin Column</u>			
B ₁ , very weak	Benzene	.48	.57
B ₂ , very weak	Methanol	.11	.08
B ₃ , weak	Methanol-isopropylamine	8.45	10.12
<u>Neutrals From Ferric Chloride</u>			
<u>Clay Column</u>			
N ₀ hydrocarbon	Pentane	79.44	81.85
N ₁ first neutral	1,2-Dichloroethane	4.75	2.84
N ₂ second neutral	Methanol	2.20	.63

^a 2.6 Percent loss apportioned throughout.^b 1.6 Percent loss apportioned throughout.

Characterization Procedures

Procedures applied to shale oil previously have been described earlier^{4,10,12-19} but will be summarized here along with procedures for oxygen types being developed. The sequence in the separation scheme is a potent characterization tool in itself and is used to supplement information obtained from more direct determinations described below. The various fractions have been given letter symbols and also names shown in table 2 to aid in discussion. Most of the fractions are actually heterogeneous with respect to acid-base character.

Nitrogen Types

Total nitrogen value, N_T, was determined with a reductive, hydrogen-nickel pyrolysis tube followed by an ammonia microcoulometer cell. A cool boat inlet system was used. Nonaqueous potentiometric titration was used to classify the nitrogen compounds^{12,13} into strong base nitrogen, N_{SB} (pK_a > 8); weak base nitrogen, N_{WB} (pK_a 8 to 2); very weak base nitrogen, N_{VWB} (pK_a 2 to -2); and nonbasic nitrogen N_N (pK_a < -2). Examples of the various nitrogen compounds which fall in these basic types are: Strong base type (alkylamines), weak base type (pyridines, quinolines, anilines, highly ring alkylated pyrroles, N-methyl indoles, etc.), very weak base type [pyrroles, indoles, amides (including cyclic amides)], and nonbasic types (nitriles, carbazoles, second nitrogen atom in some diazo-compounds, etc.). Because some pyrroles and indoles titrate only about 70 percent, they contribute to the nonbasic nitrogen also. Infrared spectrometry of dilute solution absorption near 3,480 cm⁻¹ was used to determine pyrrolic NH type, nitrogen

$N_{N-H}^{14,15}$ Colorimetry^{16,17} was used to determine α - or β -unsubstituted pyrrolic-type nitrogen N_{pyr} (excludes carbazoles).

Oxygen Types

Infrared spectrometry of dilute solutions in the free -OH region was used to classify oxygen types based on the frequency of the absorption supplemented by the fractionation sequence information. In acid fractions $3,610\text{ cm}^{-1}$ was assumed specific for phenols and $3,530\text{ cm}^{-1}$ was assumed specific for carboxylic acids.^{20,21} In fractions generated below A_3 in the sequence, the $3,610\text{ cm}^{-1}$ absorption was assumed to represent sterically hindered phenolic types which were not taken up by the anion-exchange resin. The $3,530\text{ cm}^{-1}$ region absorption for the post-acidic fractions was attributed to sterically hindered carboxylic-type compounds. Alcoholic OH, bridged phenolic OH, or some amide N-H absorptions would have been indistinguishable from that assigned to sterically hindered carboxylic OH. Spectra of the fractions were run at such dilution that Beer's law applied for the absorptions considered. Calibrations were made based on measured molar absorptivity values for the specific type compounds: Phenol and alkylated phenols, and octanoic and benzoic acids. The molar absorptivity for the sterically hindered OH-type calculations was assumed equal to that of the corresponding unhindered free OH.

RESULTS AND DISCUSSION

Distribution of Organic Material in Fractions

In table 2 the gravimetric recoveries of various fractions are compared for the two oils. The A_1 and A_2 acid fractions together represent about 3.2 percent of either oil. The AGRO fractionates equally between the two, but the ISRO is split with $A_2:A_1$ equal to 1.5. In the last acid fractions, A_3 , the AGRO:ISRO ratio is 1.7. The quantities of base fractions are similar, as are those of the hydrocarbon fractions (N_0). The N_1 , AGRO:ISRO ratio is 1.67 and the N_2 ratio is 3.5. Based on the data in table 2, the distillates show some differentiation in distribution of the very weak acid fractions. The AGRO distillate shows considerably more weak acid present than the ISRO distillate. The neutral fractions adsorbed by ferric chloride represent twice as much material in the AGRO as in the ISRO distillate. Basic and neutral hydrocarbon fractions are comparable in quantity for the two distillates.

Titration

Distillates

The titration data for the two distillates and fractions as weight percent of the distillates are shown in table 3. Total nitrogen concentrations for the two oils are the same. The AGRO titration shows 0.79 percent N_{WB} compared to 0.90 percent N_{WB} for the ISRO. The N_{VWB} value in the AGRO is 0.42 percent compared to 0.22 percent in the ISRO. The AGRO oil shows slightly less N_N than the ISRO. In summary the titratable bases are similar in amount for the two distillates. The ratio AGRO:ISRO for N_{WB} is 0.88 and for N_{VWB} 1.9 indicating lower basicity--i.e., fewer weak bases and more very weak bases--for the AGRO although there is a slightly higher N_N value for the ISRO.

Acidic Fractions

The very weak acid fractions A_1 plus A_2 AGRO:ISRO, N_{VWB} ratio is 1.8 which is in the same direction as the similar ratio for the whole distillates. In the A_2 fractions the AGRO:ISRO, N_{VWB} ratio is 10 although the amount of base represented is small. Bases in the A_3 fractions are low in quantity and comparable.

TABLE 3. - Distribution of weakly basic, very weakly basic, and nonbasic nitrogen in fractions and distillates

Fraction	Nitrogen, wt-pct of light distillate					
	Aboveground			In situ		
	N _{WB}	N _{VWB}	N _N	N _{WB}	N _{VWB}	N _N
Distillate	0.79	0.42	0.13	0.90	0.22	0.22
A ₁	.010	.056	.017	.009	.045	.023
A ₂	.013	.031	.004	.015	.003	.007
A ₃	.005	0	.005	.004	.001	.006
B ₁	.016	.012	.005	.026	.006	.005
B ₂	---	.009 ^a	---	---	.005 ^a	---
B ₃	.59	0	.033	.72	0	.023
N ₁	.014	.130	.056	.010 ^b	.085	.034
N ₂	.041	.057	.054	.013 ^b	.019	.004
N ₀	.001 ^b	.074	.038	.002	.015	.070
Recoveries						
Total in fractions ^c	.69	.37	.21	.80	.18	.17
Change in type	-.10	-.05	+.08	-.10	-.04	-.05

^a Too small to titrate; this figure is based on the total nitrogen.

^b Approaches strong-base titration characteristic potential.

^c Total nitrogen recovery AGRO = 94 percent; ISRO = 86 percent.

Basic Fractions

In the two very weak base fractions, B₁ and B₂, the overall basicity of the bases titrated is less for the AGRO fractions as in the original distillates. The weak base fractions for both oils titrate almost completely as weak bases with an AGRO:ISRO N_{WB} ratio of 0.82. A small amount of nonbasic nitrogen is present.

Neutral Fractions

The amount of nitrogen in the three neutral fractions which titrate as weak base or very weak base is remarkable. The total nitrogen, N_T, in these fractions is 0.465 weight-percent of the AGRO and 0.252 percent of the ISRO. Based on an assumption of one nitrogen atom per molecule and a molecular weight in this distillate of about 200, these figures would represent 7 weight percent of the distillate as nitrogen-containing compounds retained by the ion-exchange resins for the AGRO and about 4 percent for the ISRO distillate. The potential for polymerization of pyrroles, and more slowly indoles, in acid media²² and for their loss to cation-exchange resins²³ is well known so that the question of artifact formation of neutrals through polymerization was considered. Previous work⁴ showed less than 0.5 weight percent polymer in neutrals from cation-exchange fractionation of the AGRO. Weak base titrations in this paper approaching strong base character were observed for the AGRO-N₀ fraction and for the ISRO-N₀ and N₂ fractions. Because no strong base titration is observed for the original distillates, this suggests possible pyrrole trimer formation which would have a strongly basic nitrogen atom in addition to two pyrrolic-type nitrogen atoms. The nitrogen and oxygen types observed in the neutral fractions are treated in the following discussion as the monomeric entities the functional parts would represent.

The summation of titrations on the AGRO fractions N_0 , N_1 , and N_2 indicates them to contain about twice the basic nitrogen concentration of the ISRO neutrals. These levels represent about 26 percent of the basic nitrogen and 114 percent of the neutral nitrogen for the AGRO and about 13 percent of the basic and 49 percent of the neutral nitrogen for the ISRO.

The overall nitrogen recovery from table 3 was 94 percent for the AGRO, which is probably within the experimental error involved, but only 86 percent for the ISRO, which probably indicates a real loss of nitrogen-containing compounds to the columns. The oils showed similar decreases in N_{WB} and N_{VWB} as shown at the bottom of table 3, but the AGRO showed an apparent increase in N_N compared to a loss in the ISRO N_N . The increase in N_N for the AGRO could represent a shift in more basic nitrogen to nonbasic nitrogen. Since the shift is toward formation of neutral nitrogen, oxidation might be a suspected cause. Care was taken to prevent this by nitrogen purging. Another possible explanation is that titration characteristic potentials depend to some extent on the matrix as shown by Buell.¹⁸ We assume the latter to be the case and that the net decrease in basic nitrogen and increase in N_N in the AGRO occurred for this reason.

In summary the distillates and fractions indicate that the AGRO has lower basicity in general than the ISRO. This is consistent with a picture of a more oxidized oil since, for example, oxidation of most amines produces weaker bases or nonbasic compounds. There was appreciable loss of nitrogen in the fractionation of the ISRO, but this was not so for the AGRO. Questions of artifacts possibly introduced by the separation scheme have not been thoroughly assessed but have been discounted in the following discussions.

Pyrrolic-Type Nitrogen

Table 4 shows the distribution of pyrrolic-type nitrogen in the oils and their fractions. The notable differences here are the larger N_{N-H} in the AGRO and the large loss from this category in the fractionation.

The loss of N_{N-H} is interpreted as follows. Because the initial values of pyrrolic-type nitrogen in the AGRO distillate are $N_{NH} = 0.21$ and $N_{pyr} = 0.11$, the latter value does not include 0.10 weight percent of the distillate which represents closely the loss of N_{N-H} through the fractionation sequence. All the other pyrrolic nitrogen values in the original oils are preserved in the fractions within experimental error. The observed loss of 0.10 weight-percent of the AGRO distillate as N_{N-H} represents a real difference between these oils. One type of material this could represent is carbazoles, but these are believed to be excluded by the distillate cut points.⁴ Pyrroles or indoles with α and β substituents are an alternative interpretation fitting this boiling range.⁴ Pyrroles are known to be lost rapidly to cation-exchange resins while indoles react at a much slower rate.²³ Based on these facts, the $N_{N-H} = 0.11$ weight-percent of the oil is postulated to represent α - and β -substituted pyrroles. Using this assumption that pyrroles have been lost to the cation-exchange resin and that the pyrrolic nitrogen remaining is indole type, the ratio of N-H pyrrole nitrogen to indole nitrogen in the AGRO would be about unity but for the ISRO the ratio would be about 0.23. The N_{pyr} values are largely recovered in the fraction and probably represent mostly indole-type nitrogen assumed shown by the N_{N-H} values in the recovered fractions.

It might be expected that the higher temperature oil, the AGRO, would show N_{N-H} predominantly because as shown by Jacobson^{24,25} N-alkyl pyrroles and indoles rearrange thermally to C-alkyl isomers. Other unknowns such as the contact of the in situ oil with minerals in the post-retorting region could account for differences however. That highly substituted N-H type pyrroles appear to be lost preferentially to the columns in this work is surprising because these types are the more stable with respect to polymerization in acidic media.²² This subject requires further investigation.

TABLE 4. - Distribution of pyrrolic-type nitrogen

Fraction	Nitrogen, wt-pct of light distillate			
	Aboveground		In situ	
	N _{N-H}	N _{pyr}	N _{N-H}	N _{pyr}
Original light distillate	0.21	0.11	0.16	0.11
A ₁	.013	.017	.042	.046
A ₂	.0022	.0008	.0023	.0016
A ₃	.0016	.0002	.0003	.0001
B ₁	.0018	.0016	.0028	.0026
B ₂	.0005	.0003	.0002	.0002
B ₃	.0027	.0017	.0028	.0008
N ₁	.078	.043	.056	.035
N ₂	.0077	.0042	.0032	.0011
N ₀	.0016	.014	.024	.0023
Recoveries				
Total in fractions	.11	.083	.13	.090
Change in type	-.10	-.03	-.03	-.02

In the first acidic fractions, A₁, the AGRO shows about one-fourth of the N_{N-H} and one-third of the N_{pyr} that the ISRO fraction does. Both oils show concentration of N_{N-H} and N_{pyr} in the first neutral fraction. The AGRO N₀ fraction shows 6 times the N_{pyr} of the other oil, but the N_{N-H} values are reversed with the ISRO showing 15 times the AGRO N_{N-H} value.

Oxygen-Containing Types

Heteroatoms Per Molecule

Tables 5 and 6 show summaries of nitrogen types and hydroxylic types for the AGRO fractions and the ISRO fractions, respectively. The results are tabulated in milliequivalents per gram in the fraction. These numbers should be compared with a molal concentration of organic material of approximately 5 millimoles per gram for a distillate of M.W. 200 like the distillates we are discussing. The polar compounds in these distillates may be heavier than this but will not change the interpretation much. The total of nitrogen and oxygen atomic concentrations observed runs as high as 6.36 in the fractions indicating an average of as much as 1.3 heteroatoms per molecule in some cases. The oils appear similar in respect to the heteroatom-per-molecule values based only on nitrogen and hydroxylic oxygen.

Acid Fractions

The oils differ markedly in their hydroxylic composition in the acid fractions. It was expected from the character of the anion-exchange resin that most of the phenols would be desorbed in the first two fractions, A₁ and A₂, and any carboxylic acids would appear in A₃. For the AGRO this appears true. Except for a minor amount of phenolic type in A₃, the fraction is carboxylic acid types. On the other hand for the ISRO, A₃ contains largely phenolic types with a minor amount of carboxylic types. The appearance of major amounts of phenolic types in A₃ for the ISRO suggests these phenolic types have electron-withdrawing substituents present to enhance their acidity. Substituents²⁰ which could produce considerable enhancement of the acidity of phenols are for example formyl-, cyano-, or nitro- although no identification of these types of

TABLE 5. - Nitrogen and oxygen types in an aboveground, combustion retorted light distillate

Fraction	Wt-pct of oil	Heteroatomic type, milliequivalents per gram of fraction									
		N _{WB}	N _{VWB}	N _N	N _T	N _{N-H}	N _{pyr}	Phenolic -OH	Carboxylic -OH	Total -OH _T	Total N _T + OH _T
A ₁	1.65	0.42	2.42	0.73	3.57	0.58	0.77	2.50	0.13	2.63	6.20
A ₂	1.60	.60	1.39	.20	2.19	.10	.037	3.99	.10	4.18	6.36
A ₃	1.32	.29	0	.28	.57	.091	.013	.91	2.42	3.33	3.90
B ₁	.48	2.35	1.82	.69	4.86	.28	.25	.04	.06	.10	4.96
B ₂	.11	-	5.52 ^b	-	5.52	.31	.19	.03	0	.03	5.55
B ₃	8.45	4.98	0	.28	5.26	.024	.015	.01	0	.01	5.27
N ₁	4.75	.21	1.99	.84	3.04	1.21	.66	.57	.02	.59	3.63
N ₂	2.20	1.32	1.84	1.74	3.99	.26	.14	.04	.07	.11	4.10
N ₀	79.44	.0007	.065	.034	.10	.001	.013	0	0	0	.10

^aPartially soluble. ^bNot titrated because of small size of fraction.

TABLE 6. - Nitrogen and oxygen types in an in situ combustion retorted light distillate

Fraction	Wt-pct of oil	Heteroatomic type, milliequivalents per gram of fraction									
		N _{WB}	N _{VWB}	N _N	N _T	N _{N-H}	N _{pyr}	Phenolic -OH	Carboxylic -OH	Total -OH _T	Total N _T + OH _T
A ₁	1.32	0.50	2.43	1.26	4.19	2.29	2.51	1.45	0.058	1.51	5.70
A ₂	1.87	.56	.13	.25	.944	.089	.061	4.89	.109	5.00	5.94
A ₃	.76	.34	.084	.006	.430	.031	.014	5.02	.715	5.74	6.17
B ₁	.57	3.31	.72	.69	4.72	.36	.33	.08	.02	.10	4.82
B ₂	.08	-	4.21 ^b	-	4.21	.21	.19	.86	.05	.91	5.12
B ₃	10.12	5.11	0	.16	5.27	.020	.006	.01	0	.01	5.28
N ₁	2.84	.26	2.15	.86	3.27	1.43	.89	.09	.03	.12	3.39
N ₂	.63	1.46	2.14	.48	4.08	.37	.12	.08	.02	.10	4.18
N ₀	81.85	.002	.013	.061	.076	.021	.002	0	0	0	.08

^aPartially soluble. ^bNot titrated because of small size of fraction.

materials has been made in shale oils. The phenolic:carboxylic molal ratios are about 4 for the AGRO and about 16 for the ISRO. The A_3 fractions were of limited solubility in carbon tetrachloride so that the actual acid concentrations may have been larger than observed. If fraction AGRO, A_3 were presumed to be 100 percent carboxylic acids plus phenols, the phenolic:carboxylic ratio could be as low as 3. Higher N_N in the ISRO- A_1 fraction correlates with the greater pyrrolic nitrogen-type values observed in table 4. The N_{VWB} for the AGRO- A_2 fractions is 10 times that for the other oil. It does not correlate with N-H so this material may be amide type, including cyclic amide (pyridone, quinolone, etc.) types which have been indicated before.⁴ Additional neutral nitrogen in the AGRO- A_3 fraction could also be placed in this category for the same reasons.

Base Fractions

Small amounts of hydroxyl appear in the base fractions and are comparable for the oils except in the B_2 fractions. This fraction of either oil is such a small amount of the oil it will not be discussed further.

Neutral Fractions

No hydroxyl absorption appeared in the N_0 (hydrocarbon) fractions. The AGRO- N_1 fraction shows six times the hydroxyl absorption that the ISRO- N_1 fraction does. In addition, the AGRO- N_1 fraction is 4.75 weight-percent of the oil whereas the ISRO- N_1 fraction is 2.84 weight-percent of its oil. The AGRO- N_1 fraction represents a much larger hydroxyl concentration in the oil than the ISRO- N_1 fraction. The AGRO- N_2 fraction is 2.20 weight-percent of its oil and the ISRO- N_2 fraction is only 0.63 percent of its oil although it has slightly higher -OH concentration. The summation of hydroxyl types in the neutral fractions gives a molar ratio AGRO:ISRO of 9 in the oils with the concentration of these hydroxylic neutral types in the AGRO being only 0.03 milliequivalent/gram oil.

In the neutral fractions, nitrogen-containing types appear much more abundant than hydroxyl types. From the AGRO neutral fractions the summation of nitrogen concentrations is 0.31 meq/g oil and from the ISRO neutral fractions the nitrogen concentration is 0.18 meq/g oil either of which is over an order of magnitude above the hydroxyl-type concentrations found in either.

Nonhydroxylic Oxygen Types

The comparison of the concentrations in the distillates of each of the heteroatoms S, N, and O is shown in table 7 along with O-phenolic, O-carboxylic, and N_{VWB} found in this work. The value of phenolic plus carboxylic oxygen in the AGRO = 0.23 and in the ISRO = 0.17. This is about 77 percent of the ISRO distillate total oxygen but only about 30 percent of the AGRO distillate oxygen. Assuming N_{VWB} to contain one oxygen atom per molecule and including it in the summation of oxygen types would account for 150 percent of the ISRO distillate oxygen but only 70 percent of the AGRO distillate oxygen. This suggests a large portion of the oxygen in the AGRO occurs in other forms than we have considered. Dinneen⁵ has shown the presence of benzofuran in an AGRO-type naphtha and perhaps these types occur in this distillate also. Combinations of oxygen with sulfur could also account for the rest of the oxygen. Previous examination⁴ of the AGRO showed sulfoxides absent but other forms were not determined.

CONCLUSIONS

This paper shows that there can be considerable variation in the distribution of some nitrogen and oxygen types in two combustion retorted shale oils. It is not presently possible to infer

TABLE 7. - Comparison of heteroatomic types in 400 to 600° F distillate fractions

Species	Concentration in distillate, meq/g	
	Aboveground	In situ
S _T	0.28	0.17
N _T	.96	.96
O _T	.78	.22
<u>Oxygen Accounted For</u>		
<u>O_T</u>		
O-phenolic	.15	.15
O-carboxylic	.08	.02
N _{VWB}	.30	.16
Total	.53	.33

much about retorting mechanism from these data because of the many unknowns in the post-retorting regions in the production of the oils. The analyses of these two oils show many qualitative differences in polar fractions which could form the basis for a retorting index or parameter for comparative evaluation of shale oils.

SUMMARY

The differences in observed chemical types for the AGRO and ISRO could be interpreted largely in terms of a greater oxygen content in the AGRO. Part of this oxygen in the AGRO may be showing up as higher very weak base content (probably amides) compared to the ISRO distillate. The molal ratio of weak bases AGRO:ISRO is 0.88 and the ratio of very weak bases AGRO:ISRO is 1.9. The AGRO pyrrole:indole ratio calculated is unity, but the ISRO pyrrole:indole ratio is 0.23. The molal ratio of phenolic:carboxylic acids is about 5 for the AGRO but about 16 for the ISRO. Small amounts of hydroxyl occur in the neutral nitrogen fractions of the oils but are dwarfed by the nitrogen content. The nonhydrocarbon neutral fractions of the AGRO represent twice the concentration in the oil that the similar ISRO neutral fractions do. Hydrocarbon fractions from both oils show appreciable (0.3 to 0.5 percent) pyrrolic nitrogen concentrations. To account for the oxygen level in the AGRO, oxygen types other than hydroxylic, carboxylic, and amidic must be considered to account for 30 percent of the AGRO oxygen, but the ISRO oxygen could be accounted for this way. Although marked differences in the oils can be observed, conclusions about differences in retorting based on the heterocompound types found are tenuous because of the many questions involved in the post-retorting history of the oils.

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ABSTRACT

Crude shale oil from in situ retorting of Wyoming oil shale by the underground combustion method was hydrocracked over a nickel-molybdena catalyst in a single-pass operation at 800°F, 1,500 psig pressure, and 0.5 volume of oil per volume of catalyst per hour. The liquid product was fractionally distilled into naphtha and heavier oil. The fractions distilling above naphtha were collected at 5°F intervals and nitrogen percentages were determined on these. The distribution of nitrogen in 54 distillate fractions is reported.

NITROGEN TYPES IN SYNCRUDES FROM IN SITU CRUDE SHALE OIL

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INTRODUCTION

Crude shale oils produced by in situ combustion retorting of Green River oil shale contain more than twice as much nitrogen as high-nitrogen petroleum crudes. Because existing refineries would not be able to cope with the high nitrogen content of shale oil if it were a substantial part of the refinery feed, the National Petroleum Council (NPC) has suggested (1) that crude shale oil be upgraded at the retorting site by a process of catalytic hydrogenation to produce a premium feedstock called "syncrude."

We have already shown (2) that a premium refinery feedstock can be produced from in situ crude shale using methods suggested by the NPC. We have also determined (3) the nitrogen-compound types remaining in the finished syncrude since it would be these compounds with which a refiner would have to deal if he used a similar crude in his refinery feed.

In the NPC process, the crude shale oil is distilled to produce naphtha, light oil, heavy oil, and residuum. The residuum is processed in a delayed-coking unit to produce petroleum coke and a vapor stream. The vapor stream from the coking unit flows back to the crude distillation unit for separation into various fractions. The naphtha, light oil, and heavy oil are subsequently hydrogenated to remove nitrogen and sulfur and to reduce the viscosity and pour point of the finished syncrude.

One alternate method of preparing syncrude from crude shale oil would be to hydrogenate the total crude shale oil in a one-step process. This would not only reduce the number of processing units required at the retorting site, but could result in higher yields of liquid and gaseous products since the coking step would be eliminated.

The purpose of the present work was to prepare a syncrude of total nitrogen content comparable to that of an NPC-type syncrude produced earlier (2-3) by catalytically hydrogenating the total in situ crude shale oil in one step, and to determine the amounts and types of nitrogen compounds remaining in the finished syncrude. Yields of products, properties of the finished syncrude, and amounts and types of nitrogen compounds remaining in the one-step syncrude are compared with those of a multistep syncrude prepared by an NPC-type process.

PROPERTIES OF IN SITU CRUDE SHALE OIL

The crude shale oil used in this work, the same as that used in our previous studies (2-3), was obtained from an in situ combustion retorting experiment near Rock Springs, Wyo., during the last week of the experiment. It is considered to be a representative "steady state" oil. Properties of the in situ crude shale oil are shown in table 1.

ANALYTICAL METHODS

Standard ASTM procedures were used wherever practicable. Catalyst deposit percentages were calculated from the weights of carbon dioxide collected on ascarite when the deposits were burned with a stream of air passed through the reactor at the end of a run. Hydrogen consumption was calculated from precise measurements of the amount of hydrogen fed to the unit and that collected in the product gas. Total nitrogen values in the oils were determined with a reductive, hydrogen-nickel

TABLE 1. - Properties of in situ crude shale oil

Gravity, ° API	28.4
Nitrogen, weight-percent	1.41
Sulfur, weight-percent	0.72
Pour point, ° F	40
Viscosity, SUS at 100° F	78
Carbon residue, weight-percent	1.7
Ash, weight-percent	0.06

pyrolysis tube and an ammonia microcoulometer. Sulfur values were determined with an oxygen combustion tube and a sulfur dioxide microcoulometer. Samples were water washed. Samples for sulfur analysis were also extracted with mercury and filtered.

Nonaqueous potentiometric titration (4-7) was used to classify the nitrogen types into weak-base ($pK_a + 2$ to $+ 8$), very weak-base ($pK_a - 2$ to $+ 2$), and neutral types (nontitratable). Infrared spectrometry (6-8) was used to determine the concentration of pyrrolic N-H type nitrogen (which includes carbazoles). Colorimetry (with p-dimethylaminobenzaldehyde) (6, 9-10) was used to determine pyrroles and indoles with an unsubstituted α or β position which are termed here pyrrolic nitrogen (excludes carbazoles).

EXPERIMENTAL

The total in situ crude shale oil was hydrogenated over a presulfided, nickel-molybdenum catalyst in a fixed-bed, bench-scale unit. The crude oil was mixed with 5,000 scf of hydrogen per barrel and passed downflow over the catalyst bed at a rate of 0.7 weight of oil per weight of catalyst per hour ($W_o/W_c/hr$). The catalyst was contained in a stainless steel reactor. The temperature of the reactor was maintained at 815° F by means of a four-zone electric furnace, each zone of which was independently controlled. Pressure in the reactor was maintained at 1,500 psig by means of a backpressure regulator, and liquid products were collected in a separator maintained at 200 psig. Tail gas from the separator was metered and sampled. The hydrogenation was accomplished in a continuous 10-day run.

Liquid products were drained from the separator after each 24-hour period of operation and washed with water to remove ammonia and hydrogen sulfide before a sample was taken for analysis. Aliquot portions of the daily liquid products were combined to form the finished syncrude. A portion of the syncrude was then fractionated to obtain a C₅ - 175° F light naphtha, a 175°-350° F heavy naphtha, a 350°-550° F light oil, and a 550° F+ heavy oil. Preparation of the multistep syncrude was described in detail earlier (2) but consists basically of a distillation unit, a delayed coker, and three catalytic units for hydrogenations of heavy oil, light oil, and naphtha separately.

RESULTS AND DISCUSSION

In table 2, the yields of products from hydrogenation of the total in situ crude shale oil (one-step) are compared with yields of products from separate hydrogenation of various distillate fractions (multistep) (2). The yield of C₄+ liquid product was 104.5 volume-percent for the one-step process and 103 volume-percent for the multistep process. The yield of C₅+ liquid product was only slightly higher for the one-step process, but there was a substantial decrease in the yield of heavy oil with a corresponding increase in the yields of gas, naphtha, and light oil. Hydrogen consumption was somewhat higher for the one-step process (1,475 scf/bbl versus 1,280 scf/bbl) as the result of the increased depth of conversion.

TABLE 2. - Comparison of product yields from multistep and one-step hydrogenation of in situ crude shale oil

Product, percent of crude	Multistep		One-step	
	Weight	Volume	Weight	Volume
C ₄ + liquid product	93.81	102.99	95.27	104.54
C ₅ + liquid product	92.66	101.24	93.42	101.67
C ₅ - 175° F light naphtha	2.34	2.96	2.62	3.33
175°-350° F heavy naphtha	19.60	22.65	21.14	24.20
350°-550° F light oil	45.68	49.45	51.44	55.03
550°-850° F heavy oil	25.04	26.18	18.22	19.11
Coke (catalyst deposit)	<u>1/</u> 3.24			0.13
Hydrogen	<u>2/</u> -2.19		<u>3/</u> -2.53	
Methane	0.69		1.31	
Ethane	0.68		1.37	
Ethylene	0.03		-	
Propane	0.72		1.41	
Propylene	0.09		-	
Isobutane	0.26	0.41	0.46	0.76
Butane	0.79	1.20	1.39	2.11
Butenes	0.10	0.14	-	
Ammonia	1.57		1.69	
Hydrogen sulfide	0.62		0.75	

1/ Multistep process includes a coking step.

2/ 1,280 scf/bbl.

3/ 1,475 scf/bbl.

Table 3 shows the effect of operating time on the nitrogen contents and gravi-

TABLE 3. - Effect of operating time on nitrogen contents, denitrification rate constants and gravities of liquid product

Days on stream	Nitrogen content of liquid product, ppm	Denitrification rate constant $\ln N_0/N_t (.7)$	Gravity, ° API
1	51	5.26	44.2
2	83	4.79	43.8
3	148	4.20	43.8
4	177	4.00	43.3
5	195	3.92	43.2
6	207	3.86	43.2
7	238	3.72	43.2
8	306	3.47	43.1
9	316	3.44	43.1
10	338	3.37	43.0

ties of the liquid products. Under the conditions used in this experiment there was a significant decrease in the activity of the catalyst during the course of the run. This indicates that crude shale oil could not be processed under these severe conditions in a fixed-bed unit without frequent regeneration of the catalyst.

Properties of the syncrudes and their various distillate fractions are shown in table 4. Sulfur contents of both of the syncrudes discussed was near the lower

TABLE 4. - Comparison of syncrudes and distillate fractions from multistep and one-step hydrogenation of in situ crude shale oil

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	Multistep	One-step
Syncrude, volume-percent of in situ crude	102.99	104.50
Gravity, ° API	43.9	44.6
Nitrogen, ppm	250	225
Sulfur, ppm	5	6
Butanes and butenes, volume-percent of syncrude	1.7	2.7
C5-350° F naphtha, volume-percent of syncrude	24.8	26.3
Gravity, ° API	54.7	53.4
Nitrogen, ppm	1	83
Sulfur, ppm	8	3
350°-550° F light oil, volume-percent of syncrude	48.1	52.7
Gravity, ° API	41.5	38.5
Nitrogen, ppm	79	200
Sulfur, ppm	1	5
550° F+ heavy oil, volume-percent of syncrude	25.4	18.3
Gravity, ° API	35.6	36.2
Nitrogen, ppm	935	513
Sulfur, ppm	9	5

level of experimental uncertainty. Although sulfur could be detected down to 0.5 ppm, the significance of a few parts per million is doubtful because of difficulty in removing hydrogen sulfide and colloidal sulfur. The total nitrogen contents of the syncrudes were essentially equal; however, there were substantial differences in the distribution of nitrogen in the distillate fractions.

In table 5, the distribution of nitrogen in the two syncrudes and their distillates is shown. Although total nitrogen in the two syncrudes is comparable, it is seen that the nitrogen in the one-step syncrude occurs in significantly higher concentrations in the heavy naphtha and light oil fractions and in lower concentration in the heavy oil fraction in comparison with the multistep syncrude.

In table 6 the nitrogen distributions as percent of total nitrogen in the syncrudes and their distillates is summarized according to basic and neutral types. Almost all (86.5 percent) of the nitrogen in the multistep syncrude appears in the heavy oil, but for the one-step syncrude only about half (49.7 percent) appears in the corresponding distillate. The neutral nitrogen in these heavy oils is about 40 percent of the total nitrogen in the syncrude. This neutral nitrogen appears to be largely carbazole type in either oil. This can be inferred from table 5 by the large values for N-H type nitrogen and small values for (α or β unsaturated) pyrrolic-type nitrogen. A predominance of carbazole structures was indicated by mass spectrometry in the characterization of the multistep heavy oil (3), but mass spectrometry was not used in characterization of the one-step syncrude. The fate of the neutral nitrogen then appears similar in either multistep or one-step processing; the neutral type concentrating in the heavy oil while other, more readily hydrogenated types react.

As shown in table 6 the amounts of basic nitrogen (weakly basic plus very weakly basic nitrogen) relative to the total nitrogen is similar for the two syncrudes, but differs markedly for the corresponding distillate fractions in the two oils as does the occurrence of primary and secondary amines. In the multistep

TABLE 5. - Nitrogen distribution in syncrudes and their fractions

Fraction	Total nitrogen in fraction, ppm	Nitrogen-type, weight-percent of nitrogen in fraction				
		Weak base	Very weak base	Neutral	Pyrrolic N-H	Pyrrolic
Syncrude ^{1/}	250	47.9	12.1	40.0	9.9	1.1
Syncrude ^{2/}	225	54.2	10.2	35.6	21.8	4.0
Light naphtha ^{1/}	0.5	-	-	-	-	-
Light naphtha ^{2/}	0.5	-	-	-	-	-
Heavy naphtha ^{1/}	0.8	-	-	-	-	-
Heavy naphtha ^{2/}	83	95.2	3.6	1.2	0	1.2
Light oil ^{1/}	79	100	0	0	0	0
Light oil ^{2/}	200	80.0	8.0	12.0	0	3.5
Heavy oil ^{1/}	935	37.4	12.2	50.4	39.3	4.2
Heavy oil ^{2/}	513	14.2	11.7	74.1	60.4	3.1

^{1/} Multistep.^{2/} One-step.

TABLE 6. - Basic and neutral nitrogen distribution in syncrudes and their fractions

	Nitrogen, percent of total in syncrude			
	Total	Basic	Neutral	I°, II° amines ^{1/}
Syncrude ^{2/}	100	60.0	40.0	0
Syncrude ^{3/}	100	64.4	35.6	3.5
Light naphtha ^{2/}	0	0	0	0
Light naphtha ^{3/}	0	0	0	0
Heavy naphtha ^{2/}	0	0	0	0
Heavy naphtha ^{3/}	10.6	10.5	0.1	2.2
Light oil ^{2/}	13.5	13.5	0	0
Light oil ^{3/}	39.7	34.9	4.8	2.0
Heavy oil ^{2/}	86.5	42.9	43.6	0
Heavy oil ^{3/}	49.7	12.9	36.8	0

^{1/} I° and II° amines included in basic nitrogen.

^{2/} Multistep.

^{3/} One-step.

syncrude, the weakly basic nitrogen compound types were shown to be largely pyridines, and the very weakly basic nitrogen compound types were shown to be largely pyrroles and indoles by a combination of techniques including mass spectrometry. Although mass spectrometry was not used in characterization of the one-step syncrude, the compound types are probably similar.

Presence of large amounts of nitrogen in the light oil and heavy naphtha of the one-step syncrude can be attributed to hydrocracking and thermal cracking reactions in the heavy oil and residual portions of the crude. Buildup of nitrogen compounds in the lighter oil products from heavy oil hydrogenation in the multistep syncrude production was observed in earlier work (3). This lighter oil produced from the heavy oil hydrogenation is then hydrogenated in the various lighter oil reactors in the multistep process (2). The basic types are readily converted to ammonia as found by others (4, 12) and as evidenced by the relatively mild conditions required to reduce the nitrogen content in the fractions boiling below 550° F to the low values in table 6 (2).

The occurrence of small amounts of primary and secondary amines in both the heavy naphtha and light oil fractions from the one-step syncrude is consistent with the work of Brown (11) who found anilines made up nearly one-third of the tar bases from a recycle, hydrocracked shale-oil naphtha. None of these amines were found in the multistep syncrude product although anilines were identified in intermediate fractions (light oil products from the heavy oil hydrogenation unit). In the multistep process these amines are removed readily in the lighter oil reactors as part of the basic types which were discussed in general earlier.

SUMMARY

Total crude shale oil produced by underground combustion retorting was hydrogenated in one step over a nickel-molybdenum catalyst at an operation temperature of 815° F, an operating pressure of 1,500 psig, and a space velocity of 0.7 W₀/W_c/hr. A high yield (104.5 volume-percent) of synthetic crude oil, called a one-step syncrude, containing 225 ppm total nitrogen was attained. Hydrogen

consumption was 1,475 scf/bbl. A combination of microcoulometry, nonaqueous potentiometric titration, colorimetry, and infrared spectroscopy was used to determine the amounts and types of nitrogen compounds present in the syncrude and its various distillate fractions.

Light naphtha comprised 3.2 percent of the syncrude and contained no nitrogen. Heavy naphtha comprised 23 percent of the syncrude and contained 83 ppm nitrogen. The light oil comprised 53 percent of the syncrude and contained 200 ppm nitrogen, and the heavy oil comprised 18 percent of the syncrude and contained 513 ppm nitrogen.

The nitrogen compounds in the naphtha were shown to be 95 percent weak base of which 6 percent were primary and secondary amine types, 4 percent very weak base, and 1 percent neutral compounds. Nitrogen compounds in the light oil were shown to be 80 percent weak base of which 5 percent were primary and secondary amine types, 8 percent very weak base, and 12 percent neutral compounds. The nitrogen compounds in the heavy oil were shown to be 14 percent weak base, 12 percent very weak base, and 74 percent neutral compounds. More than 80 percent of the neutral compounds were largely carbazole types.

The one-step syncrude produced in this work was compared with a multistep syncrude of comparable total nitrogen content and basic and neutral nitrogen compound-type content produced earlier by a process suggested by the NPC. These syncrudes contained comparable amounts of neutral nitrogen-type compounds in their heavy oil fractions. Basic nitrogen-type compounds in the one-step syncrude were distributed in much larger amounts in the light oil and heavy naphtha fractions than in the corresponding multistep syncrude fractions. There was no nitrogen in either of the light naphtha fractions. The distribution of basic nitrogen into the lower boiling syncrude fractions is interpreted as a consequence of cracking of the heavy oil and residual portions of the crude oil subjected to the one-step process. The basic cracking products are readily denitrified in the lighter oil reactors in the multistep process.

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NITROGEN AND SULFUR IN RAW AND REFINED SHALE OILS

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INTRODUCTION

Raw Green River Formation shale oils contain significantly higher concentrations of some heteroatoms than most petroleum fractions of a similar distillate range. The nitrogen content of shale oils often runs twice that in a petroleum and therefore may require special refining methods. Removal of heteroatoms from shale oil is important because of (1) the potential for air pollution from their combustion products and (2) the susceptibility of modern refining catalysts to degradation, especially by nitrogen compounds. In addition to high heteroatom content, shale oils by and large have pour points too high for pipelining. In a shale-oil industrial process some sort of upgrading or partial refining is usually planned for reducing heteroatom content and improving fluidity to attempt to make shale oil compatible with existing petroleum processing facilities.

This paper reviews and discusses the work since the first Synthetic Liquid Fuels Act (1944) relating to heteroatom and heterocompound content of shale oils produced from Green River Formation of Colorado, Utah, and Wyoming oil shales. The work includes heteroatomic composition data for raw shale oils (crudes and distillates from various retorting processes) and their products in various stages of refining. Refining methods to be discussed include early upgrading processes involving distillation, delayed-recycle coking, thermal visbreaking, and acid and base or solvent extraction. Finally, modern hydrodenitrogenation (HDN) work with shale oil and related materials will be presented and heterocompound-type data for some refined and partially refined products will be discussed along with related analytical techniques.

It is apparent in reviewing the refining of shale oil that the nitrogen level has been the primary index of refining with respect to heteroatom content. This is not only because of the severe nitrogen effect in catalyst degradation¹ but also because of the persistence of nitrogen relative to sulfur and oxygen in the course of modern refining. For this reason data on sulfur and oxygen heterocompounds in shale oils are lacking in most cases.

DISCUSSION

Effect of Retorting Process on Heteroatom Content

One advantage in use of shale oil as a feed is that once a set of retorting parameters is found giving a desired and stable retorting operation the feed produced could be quite constant in its properties. All shale oils are not alike, however. Jensen² has shown that retorting processes in which the oil shale is more slowly heated in general correlate with oil products having increased amounts of naphtha plus light distillate fractions. In these fractions the aromatic content remains constant, but the saturate-olefin ratio increases. An approximate index to these effects is the specific gravity or pour point of the oil. In table 1 we see properties of crude shale oils produced by various retorting methods arranged from top to bottom in order of decreasing specific gravity or pour point. We see that the nitrogen level decreases in the same order but that the sulfur level only decreases appreciably in the lower half of the table.

As pointed out by Jensen² the retorting parameters that control the character of shale oils, largely, are shale size, combustion zone velocity, and effective retorting temperature. If this is

TABLE 1. - Properties^a of crude shale oils

Retort type	Retorting Index or T °F	Specific gravity, 60/60° F	Pour point, °F	Nitrogen, wt-pct	Sulfur, wt-pct
Gas combustion ³	1,200 ^b	0.943	85	2.13	0.69
Fischer assay ³	900 ^b	.918	70	1.95	.64
150-Ton batch ²	---	.909	60	1.59	.94
USBM in situ-4 ²	---	.885 ^d	40	1.36	.72
Equity Oil in situ ⁴	750 ^c	.825 ^d	-20 ^d	.53	.49

^a - References in table refer to properties of oils. ^b - Retorting index. ^c - Temperature of injected fluid. ^d - Properties of oil produced in laboratory simulation of process.⁴

carried a step further, it can be pointed out that these are not independent parameters and that effective retorting temperature itself may suffice to classify retorting methods.

Jacobson^{5,6} has defined a retorting index with dimensions of temperature which relates to the severity of oil-shale pyrolysis. The index is derived from the ethylene:ethane ratio in the retort product gas. The retorting index is listed in table 1 for the gas combustion retort and the Fischer assay retort along with the measured temperature of the injected fluid used in the Equity Oil in situ process. We see at least qualitatively that these temperatures are in a systematic order.

To see that the oils with unknown retorting temperatures or indexes also probably fall in a logical order based on particle size, let us consider each process very briefly. The gas combustion retort,⁷⁻¹¹ heated by internal combustion is fed crushed-screened shale of about 3-inch dimensions. The Fischer assay retort^{7,12} uses small sized shale crushed to pass 8 mesh screen but is externally heated at a controlled moderately low rate. The 150-ton batch retort^{7,13-15} uses mine-run shale with blocks as large as 3 ft x 4 ft x 5 ft and is heated by internal combustion. The USBM in situ oil¹⁶⁻¹⁸ was a combustion-retorted oil produced in fractured shale between injection and recovery wells. The Equity Oil in situ oil^{4,19} was produced by recycling of hot natural gas, at a controlled temperature, into an oil-shale formation. All of the combustion-type retorts were of the forward burning type where gas plus oil moves countercurrently to oil shale. Except for the Fischer assay retort which is a controlled temperature retort, the increase in particle size is down table 1 corresponding with decreasing heating rate. It is probable that the USBM in situ experiment with poorly controlled combustion had a higher effective temperature than the controlled nonoxidative Equity Oil process. Very high temperature retorted oils²⁰⁻²⁵ which by their very high aromatic content indicate a high degree of pyrolysis of the oil itself do not fit the above oversimplified pattern.

In summary, nitrogen and sulfur levels are both affected by the retorting method. Nitrogen level varies over a wider range than sulfur level and follows the specific gravity, pour point, and probably effective retorting temperature down for these oils. There is then potential for control of the nitrogen level in a crude shale oil through retorting. Whether the method of retorting adopted might be an economic approach to denitrogenation will not be pursued in this review. It depends undoubtedly on many factors, chief of these being probably the desired end use of the oil, whether for petroleum-type feedstock, direct fuel production or for chemicals, and the efficiency of resource recovery sought.

Composition of Raw Shale Oils

Much of the early shale-oil characterization work was on a shale oil from an NTU (Nevada-Texas-Utah) retort which was an aboveground internal combustion batch-type retort.²⁶ Cady and Seelig²⁷ have shown that an NTU crude may contain as much as 61 percent heterocompounds of which about 60 percent are nitrogen compounds, 10 percent sulfur compounds, and 30 percent oxygen compounds. Thus only 39 percent of this oil is hydrocarbons. These proportions will vary some depending on the retorting scheme; but in any case, the heterocompounds form a significant part of the potential source of hydrocarbons. The work in identification of specific heterocompound types and heterocompounds in an NTU shale-oil naphtha²⁸ and in a heavy gas oil²⁹ has been summarized by Dinneen and others.³⁰⁻⁴⁰ Others studying light gas oil fractions and other distillates have supplemented this work.⁴¹⁻⁴³ The naphtha and heavy gas oil represent the extremes of molecular weight in the distillates. Having nitrogen compound-type analyses for these extreme fractions with supplementary information on light distillate fractions allows interpolation to aid in compound-type assessment throughout the shale-oil distillate range. Sulfur and oxygen compound-type analyses have been done only for the naphtha distillate region.

In the following generalized discussion, the description of a compound type will be construed to include also homologous and benzologous series members depending on boiling range--e.g., pyridinic-type N includes pyridine, quinoline, acridine, alkylpyridines, etc.

Sulfur

In table 2⁴⁴ we see that for a crude shale oil the sulfur distribution is rather uniform throughout the boiling ranges but that nitrogen is more concentrated as the fractions get heavier. We have already seen in table 1 that the type of retorting seems to have only a second-order effect on sulfur level in the crude. The refractory nature of the sulfur⁴⁵ may be accounted for by the fact that most of the sulfur is in thiophene types^{28,44} as shown in table 3 for a naphtha fraction.

Oxygen

The oxygen in a shale-oil crude may run 0.5 to 2 percent. Much of the oxygen in a naphtha,²⁸ light distillate,⁴³ and gas oil²⁹ appears as phenols with minor amounts of carboxylic acids. Benzofuran was found in small amounts in the nonacidic portion of the naphtha.²⁸ It was shown

TABLE 2. - Sulfur and nitrogen contents of distillates from a Green River
Formation crude shale oil⁴⁴

Fraction	Nominal boiling range, °F	Nitrogen, percent by wt	Sulfur, percent by wt
Naphtha	<400	1.17	0.77
Light distillate	400-600	1.24	.83
Heavy distillate	600-800	1.60	.79
Residuum	>800	2.04	.70

that light distillates from different retorting processes can vary in their oxygen content and its distribution.⁴³ For one in situ produced oil, oxygen appears to be accounted for largely in the tar acids. For one aboveground retorted oil it appeared that two-thirds of the oxygen was unaccounted for by tar acids implying the presence of other forms of oxygen possibly amidic type,^{41,43} or other as yet unclassified types.

TABLE 3. - Type sulfur in Green River Formation shale-oil naphtha⁴⁴

Sulfur type	Percent of total sulfur
Elemental	0
Thiol	4
Disulfide	2
Sulfide (includes cyclics)	19
Residual (includes thiophene type)	75

Nitrogen

The principal nitrogen-containing species in shale oils are pyridine types and pyrrole types. In pyridinic types the single aromatic ring type appears to predominate over multiple ring types through wide distillate ranges. In pyrrolic types multiaromatic rings tend to predominate as boiling range increases.^{29,41} Small amounts of amides,⁴¹ arylamines,⁴⁶⁻⁴⁸ and nitriles^{28,35} have been detected. Much of the nitrogen in shale-oil distillates is basic enough to titrate in acetic anhydride ($pK_a > -2$)^{28,41-43} and be extracted by acidic agents as shown in table 4.⁴² In addition appreciable acidic material containing oxygen or nitrogen is titratable in pyridine ($pK_a < 12$) and is extractable from the lighter distillates by basic reagents as shown. The relative amounts of various nitrogen types and their basicities observed for a shale-oil light distillate are shown in table 5.⁴¹

TABLE 4. - Polar materials by different methods for a 150-ton batch retort shale oil⁴²

Method	Nominal distillate cut		
	Naphtha IBP to 400° F	Lt. distillate 400° F to 600° F	Gas oil 600° F to 1,000° F
<u>Bases, wt-pct</u>			
Titration: Weak, ^a very weak ^b	7.1, 3.6	13.1, 2.4	27.9, 0.0
Ion-exchange extraction	10.2	12.8	24.3
Aqueous extraction	11.2	11.5	12.0
<u>Acids, wt-pct</u>			
Titration: Weak, ^c very weak ^d	1.0, 3.9	0.8, 5.6	0.3, 8.0
Ion-exchange extraction	4.2	3.3	1.1
Aqueous extraction	5.0	3.7	1.2

^a $pK_a = +8$ to $+2$. ^b $pK_a = +2$ to -2 . ^c $pK_a = +3$ to $+10$. ^d $pK_a = +10$ to $+12$.

Products from Early Refining Processes

Because of the waxy, viscous nature of shale oils from conventional retorting processes and the high pour point and heteroatom content along with the low light-end content, it was apparent from the outset that some sort of hydrocarbon-conversion process was required for shale-oil utilization. Early work centered on thermal processing (visbreaking, recycle cracking, and coking) along with chemical treatment to remove objectionable compounds in an attempt to improve gasoline and distillate fuel content and stability of shale oil.⁴⁹⁻⁵⁴ These methods were chosen because of the

TABLE 5. - Summary of nitrogen-type analysis of a shale-oil light distillate (400° to 600° F)⁴¹

Nitrogen type	Percent of total nitrogen
Weak bases (pKa = +8 to +2)	
Alkylpyridines	43
Alkylquinolines	22
Very weak bases (pKa = +2 to -2)	
Alkylpyrroles (N-H)	10
Alkylindoles (N-H)	9
Cyclicamides (pyridones, quinolones)	3
Anilides	2
Unclassified	7
Nonbasic (pKa < -2) corrected for pyrroles and indoles	4

availability of these processing facilities in all refineries, because of the poor economic aspect of hydrogenation at the time, and the lack of suitable catalysts which could stand up to the high nitrogen concentrations encountered in shale oil.

Thermal Methods

Visbreaking of shale oil or cracking with recycle can produce a low pour point shale oil with increased light end content. Recycle delayed coking can further increase the light end content as shown in table 6 but does not affect the nitrogen and sulfur concentrations appreciably.⁵⁴

TABLE 6. - Recycle delayed coking of crude shale oil to various endpoints⁵⁴

	Crude feed	Nominal distillate endpoint		
		650° F	750° F	850° F
Yields, vol-pct	--	77	87	89
Sulfur, wt-pct	0.74	0.63	0.61	0.63
Nitrogen, wt-pct	2.01	1.65	1.90	1.95
		<u>Light end yields</u>		
IBP-350° F, vol-pct	1.5	5.5	9.0	19
350-550° F	18	87	36	36

Chemical Methods

Chemical treatment of shale oils can be very effective in nitrogen removal. One such treatment consisting of successive contacting at 100° F with 15 weight-percent NaOH, 20 weight-percent H₂SO₄, 100 percent H₂SO₄, and then neutralization with 3 volume percent NaOH produced a diesel fuel from a shale-oil light gas oil as shown in table 7.⁵⁰ The sulfur level, however, is nearly unaffected. Although similar treatment of naphtha fractions may produce very low

TABLE 7. - Result of chemical treatment^a of shale-oil recycle delayed-coker distillate light gas oil (400° to 670° F)⁵⁰

	Raw oil	Treated oil (diesel fuel)
Yield, vol-pct	100	67.0
Sulfur, wt-pct	0.84	0.74
Nitrogen, wt-pct	1.66	.085
Tar acids, vol-pct	3.4	.3
Tar bases, vol-pct	13.0	0

^a Treatment consists of 15 percent by weight NaOH, 20 percent by weight H₂SO₄, 100 percent H₂SO₄ (22.8 lb/bbl), and 3 volume percent NaOH to neutralize, then redistill to restore end-point. Treating temperature about 100° F.

nitrogen gasolines, these may still have a few tenths percent sulfur present. Diesel fuels from various solvent extractions of light oils showed greatly improved nitrogen levels with little effect on sulfur levels much the same as acid base treated oil in table 7.

The loss of distillate shown in table 7 illustrates a problem with chemical refining of shale oil. Undoubtedly quite effective nitrogen and oxygen compound removal could be achieved with various reactants or solvents, but it is unlikely that improvement in sulfur level would be obtained because of the chemical similarity of thiophene-type compounds to the hydrocarbon matrix. If all heterocompounds were removed from a crude shale oil, as much as 60 percent of the oil might be removed.²⁷

Summary

It was shown by the Bureau of Mines in 1949⁵¹ that adequate gasolines and diesel fuels could be produced from shale oil by methods like those just discussed. However, there were at least three good reasons for continuing research in refining of shale oil. First, the losses in raw material involved in extraction of heterocompounds represent great waste unless a ready use exists for the extracted materials. Secondly, the demand for very low nitrogen stocks for refining to high octane fuels was increasing. Finally, the pressure from an environmental standpoint for extremely low sulfur fuels was increasing steadily.

Products from Modern Refining Processes

Fortunately a by-product of the demand for higher octane fuels was hydrogen from petroleum catalytic reforming processes. The economics of hydrogen utilization began to look favorable as a means of improving the quality of shale oils and the research emphasis swung to hydrogenation. In 1947 Union Oil was successful, on a pilot plant basis, in catalytic hydrosulfurization of high thiophenic sulfur-type coker distillates from Santa Maria Valley crude petroleum.⁵⁵ Since then, aided by the increasing availability of hydrogen, much work has been done in refining shale oil via hydrogenation one way or another.⁵⁶⁻⁷⁵ Shale-oil crude was analogous to this petroleum crude in that sulfur was present largely as thiophenes and distributed uniformly throughout the distillate ranges.⁵⁵ As it turned out, both sulfur and nitrogen could be removed from shale oil effectively by catalytic hydrogenation. Production of potentially high quality fuels and refinery feedstocks has been achieved in many cases.

The question of which method of HDN is best of course depends on the individual case--i.e., what is the feed and what are the desired products. Knowledge of the types and kinetics in

HDN of heterocompounds remaining in refined and partially refined shale oils could be of value in optimizing refining processes. Nitrogen level alone is only a partial criterion of the degree of hydrogenation that has taken place. Various deleterious heterocompounds appear to be removed at different rates for a given set of conditions as discussed below. To date little data concerning the nature and reactivity of the heterocompounds in refined shale oils have appeared in the literature of shale-oil refining.

Sulfur and Oxygen

In the hydrodesulfurization of Santa Maria Valley petroleum crude by Union Oil, all types of sulfur present (mercaptan, sulfide, and thiophenic) appeared to be removed at the same rate.⁵⁵ Little compound-type information relating to hydrodesulfurization or hydrodeoxygenation has been reported in shale-oil refining studies however. This is probably because it has been found in refining of shale oils by catalytic hydrogenation that both sulfur and oxygen are removed before desired nitrogen levels are attained. In cases where results suggest otherwise, it is not always apparent whether analytical interference from elemental sulfur might not have been a factor. Elemental sulfur is formed readily as an interference by air oxidation of hydrogen sulfide. Inadvertent air contact with hydrogenated distillates before thorough washing has been accomplished may complicate evaluation of low organic sulfur levels. (Elemental sulfur may be removed from oils by extraction with metallic mercury⁷⁶⁻⁷⁷ or in some cases with aqueous sulfite solution.⁷⁸) In addition, direct low-level oxygen analyses are not readily available in most laboratories. From these properties of sulfur and oxygen, it can be understood why nitrogen level has been the index usually used in shale-oil heterocompound removal studies.

Nitrogen

In an attempt to work out some of the HDN reaction kinetics, several shale-oil HDN studies have been made in which nitrogen-type analyses were presented.^{46-48,73,75,79-81} Studies have been made on pure nitrogen compounds occurring in shale oils and also on low-level nitrogen oils "spiked" with some of these nitrogen compounds.⁸²⁻⁸⁵ Work in this area has been aided by the simple nitrogen-type analysis described by Koros, et al.,⁴⁶ extended by Silver, et al.^{47,48} and by Poulson, et al.^{41,81}

This analytical method for nitrogen types uses elemental analysis, nonaqueous titrimetry, infrared spectrophotometry, and visible colorimetry to define several nitrogen types: 1° and 2° alkylamine, 3° amine (pyridine and other), arylamine, pyrrolic N-H, α - or β -unsubstituted pyrrolic (excluding carbazoles), amide, and miscellaneous very weak base and nonbasic nitrogen types. Further subdivisions are possible depending on which groups are represented in a given sample. As hydrogenation progresses, oxygenated types disappear so rapidly that specific compound-type assignments become simpler. Some examples of uses of this analysis and the nature of hydrodenitrogenated shale oils are shown below followed finally by a summary of the principal nitrogen types in a premium shale-oil syncrude having 0.025 percent nitrogen.

Pyridines Versus Pyrroles

This analysis has been used to resolve a fundamental conflict in shale-oil refining literature; which is easier to hydrodenitrogenate, pyridinic types or pyrrolic types? Researchers were split about equally on each side of this question. Using an analytical scheme similar to the one just described, Frost and Jensen⁷³ were able to rationalize the conflicting reports. Working with crude shale oil over a wide range of temperature and hydrogen pressure, they showed denitrogenation of pyridinic types was faster than for pyrrolic types at low temperature and pressure, but the other way round for more severe conditions of temperature and pressure.

Anilines in Shale Oils

The reaction sequence for denitrogenation of indoles and carbazoles proposed by Flinn, et al.^{83,84} contains approximately a dozen competing or consecutive reactions. Reactants, intermediates, and products run the gamut from nonbasic to strongly basic nitrogen types. Anilines are postulated as intermediates as they are also in a denitrogenation sequence proposed for quinolines by Doelman and Vlugter⁸⁵ and Koros, et al.⁴⁶ Anilines would arise from saturation of the heteroring in a fused ring compound followed by rupture of the bond between nitrogen and the aliphatic carbon.

One-Step HDN

Although anilines themselves have been shown to be readily hydrodenitrogenated,⁸³⁻⁸⁵ they have been observed in severely hydrodenitrogenated shale oils. Brown⁷⁹ found that 33 percent of the tar bases in a hydrocracked recycle shale-oil naphtha were anilines at 95 percent denitrogenation. Koros, et al.,⁴⁶ Silver, et al.,^{47,48} and Frost⁷⁵ found a few percent aniline-type nitrogen in shale oils which had up to 98 percent denitrogenation levels. All these results were based on one-step HDN processes whereby anilines formed by the processes just described above would appear directly in the products, probably as lighter boiling compounds as a result of hydrocracking.

Multistep HDN

In addition to the one-step syncrude described above, Frost, using a multistep HDN process with the same crude shale-oil feed and denitrogenating to a similar level, produced a syncrude with a different nitrogen-type distribution.^{74,81} The multistep process, based on an NPC proposed scheme,⁸⁶ involves continuous catalytic hydrogenation of three individual distillate fractions from a crude shale oil with the inclusion of products from delayed coking of the residuum in the distillate fractions. Anilines were completely absent from this syncrude product but did show up in intermediate products.

In table 8 the heteroatom composition of these two syncrudes is reviewed, as discussed by

TABLE 8. - Nitrogen and sulfur in shale-oil syncrudes and distillate fractions⁷⁵

	Nitrogen, ppm		Sulfur, ppm	
	Multistep	One-step	Multistep	One-step
Syncrude	250	225	5	6
Naphtha	1	83	8	3
Light oil	79	200	1	5
Heavy oil	935	513	9	5

Frost⁷⁵ in this symposium, and is compared through the distillate ranges. Light nitrogen compounds are virtually absent from the multistep syncrude illustrating the difference of a multistep process compared to a single-step process.

Premium Syncrude

Residual nitrogen types in a shale-oil premium syncrude (multistep syncrude above) heavy oil (550° to 850° F) were determined by Poulson, Frost, and Jensen⁸¹ using the above-described classification scheme supplemented by mass spectrometry. This heavy oil contained 935 ppm nitrogen which was 90 percent of the total nitrogen in the syncrude. The total nitrogen concentration

in the whole syncrude was 250 ppm and resulted from over 98 percent nitrogen removal from the crude shale-oil feed. The general nitrogen-type analyses are shown in table 9. In pyrrolic types,

TABLE 9. - Summary of nitrogen types in a heavy oil (550° to 850° F)^a from a multistep shale-oil syncrude^b

	N, pct of total in oil
<u>Pyrrolic-type nitrogen</u>	
Three aromatic rings	30
One or two aromatic rings	25
<u>Pyridinic-type nitrogen</u>	
Two aromatic rings	15
One aromatic ring	30

^a Total N = 935 ppm. ^b Total N = 250 ppm.

three aromatic ring compounds (carbazoles) predominate and in pyridinic types one aromatic ring compounds (pyridines) predominate, much as in a raw shale-oil heavy gas oil.²⁹ A slight olefin interference makes the exact pyridine:quinoline ratio somewhat uncertain in table 9, however.

In table 10 the neutral and very weak-base nitrogen types are summarized for this heavy oil which represents 90 percent of the nitrogen in the syncrude. Pyrroles and indoles appear to be N-unsubstituted and highly ring-alkyl substituted. Carbazoles in this oil are about evenly split between N-substituted and N-unsubstituted types.

TABLE 10. - Summary of neutral and very weak base nitrogen types in the heavy oil (550° to 850° F)^a from a multistep shale-oil syncrude^b

Nitrogen-type compounds	N, pct of total in fraction
<u>N-unsubstituted pyrroles (or indoles)</u>	29.0
α - or β -unsubstituted	6.8
α - or β -substituted	22.2
<u>Carbazoles</u>	71.0
N-unsubstituted	34.4
N-substituted	36.6

^a Total N = 935 ppm. ^b Total N = 250 ppm.

In summary HDN is effective in heteroatom removal from shale oils and its use has been and is being studied widely. Optimum processing conditions for denitrogenation of shale oils depend on the individual case but probably have not been determined for many situations. Little information on nitrogen types in refined or partially refined shale oils has been reported. A relatively simple analytical scheme can produce nitrogen-type compound data of aid in mechanistic interpretations of denitrogenation reactions in shale oils.

SUMMARY

Crude Green River Formation shale oils contain large amounts of heterocompounds containing nitrogen, sulfur and/or oxygen. Shale oils produced in low temperature retorting processes seem to have lower nitrogen levels paralleling lower specific gravities and pour points. The effect of retorting on sulfur level is not as clear. Sulfur occurs principally as thiophenic-type compounds. Oxygen occurs mainly as phenols with minor amounts as carboxylic acids, amides, ethers, or other unidentified types. Nitrogen occurs principally as pyridinic type and pyrrolic type with small amounts of amide types, nitriles, and other unidentified types. Refining of shale oil by thermal methods and chemical or solvent extraction processes reduces nitrogen levels appreciably, but sulfur level is not affected much. Refining of shale oil by processes involving hydrogenation can be effective in producing extremely low level nitrogen, sulfur, and presumably oxygen fuels and feedstocks.

The susceptibility of oils to HDN depends on the nature of the nitrogen compound types present and the hydrogenation scheme employed. The nature of the nitrogen compound types remaining at low levels after upgrading of shale oil gives evidence of the reaction mechanisms involved. Some available analytical techniques can give nitrogen compound-type information relating to mechanisms of hydrodenitrogenation.

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